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Temporal Changes in Contaminant Levels in Brown Pelican Eggs Collected in 1993 and 2005 from West Anacapa Island, California

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Photo by National Park Service

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Abstract

In the late 1960s, severe reproductive impairments were reported for nesting colonies of the California brown pelican (*Pelicanus occidentalus californicus)* in the Southern California Bight. In 1970, West Anacapa Island (WAI) was home to the last active colony in the California portion of the Southern California Bight (SCB), and that colony produced as few as 1 fledgling from 552 nest attempts. The low fledging rate was due to poor hatch rates caused by eggshell thinning and breakage of eggs. Eggshell thinning and possibly other impairments were attributed to exposure to organochlorine (OC) compounds, primarily DDE (a breakdown product of the pesticide DDT), and PCBs discharged into coastal waters and accumulated in the tissues of fish consumed by pelicans. Data on eggs collected between 1970 and 1992 indicate that exposure by WAI pelicans to OC pesticides and PCBs started to decline in the 1970s when uses of many OC compounds in the United States were either curtailed or banned. There were also corresponding increases in eggshell thickness and overall productivity of the WAI pelican colony. Data on contaminant exposure by WAI pelicans had not been collected since 1992, when although thicker, eggshells still exhibited some thinning, concentrations of DDE in individual eggs still exceeded thresholds for crushing, and nest productivity was still below what was expected.

This study was conducted to update the data on contaminant exposure by WAI pelicans, and to evaluate temporal trends and the potential role of contaminants as a limiting factor for productivity in the WAI colony. To do so, viable eggs collected in 1993 and 2005 were analyzed for numerous classes of contaminants including legacy OCs (e.g., DDE and PCBs), metals and newer use contaminants (PBDEs). Results of chemical analyses show that eggs of WAI pelicans continue to have measurable levels of numerous organic and inorganic contaminants. However, of all the contaminants considered, DDE and PCBs continue to dominate. Geometric mean DDE concentrations decreased from 1,319 ng/g fw in 1993 to 609 ng/g fw in 2005. These concentrations are orders of magnitude lower than concentrations observed with intact eggs collected in 1969/70 (means ~30,000 ng/g fw). They are also below the threshold of 3,000 ng/g fw associated with eggshell thinning and breakage. Concentrations of PCBs declined from 1,168 ng/g fw in 1993 and 710 ng/g fw in 2005, and are 4 to 5 times lower than 4,500 ng/g fw measured in eggs from 1969. The differences between 1993 and 2005 concentrations for both DDE and PCBs are statistically significant ($p = 0.0002$ and 0.0033, respectively). While fluctuations in contaminant levels may be attributed to a variety of factors, the decreases in DDE and PCB concentrations appear to reflect long-term declines of these compounds in the system. The newer use compounds PBDEs were detected in pelican eggs at concentrations exceeded only by DDE and PCBs. Concentrations of PBDEs showed no statistically significant change between 1993 (mean = 116 ng/g fw) and 2005 (mean = 132 ng/g fw). The implications of these concentrations regarding adverse effects are unknown. Given their rank relative to DDE and PCBs, and uncertainties about exposure and effect levels, PBDEs are considered contaminants of concern for WAI pelican eggs. Although low, concentrations of three OC compounds (pentachloro anisole, tetrachlorobenzenes and heptachlor) increased between 1993 and 2005. As such, these compounds are considered contaminants of potential concern for WAI pelican eggs as

well. The mean shell thickness for eggs collected in 2005 (0.59 mm) is significantly greater ($p<0.05$) than that for eggs collected in 1993 (0.54 mm), and are not significantly different from eggs collected before 1943 (0.572 mm). Productivity of WAI pelicans has improved substantially since the late 1960s. However, the long-term average for number young fledged per nest attempt (0.65) is still below the long-term mean of 1.0 observed with brown pelican colonies outside the SCB. While factors such as food supply may play a role in the apparently low number fledged per nest attempt, contaminants are present and subtle effects associated with contaminant exposure may not be completely ruled out as contributing factors.

Keywords: Brown pelican, Southern California Bight, Organochlorines, DDT, PCBs, PBDEs, metals, *Pelicanus occidentalus californicus*

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The findings and conclusions in this report are those of the author(s) and do not necessarily represent the views of the U.S. Fish and Wildlife Service.

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Acronyms/Abbreviations

AAS - atomic absorption spectrometry
ACF - Analytical Control Facility
Ag - silver
Al - aluminum
As - arsenic
B - boron
Ba - barium
Be - beryllium
BHC - benzene hexachloride
Ca - calcium
cc - cubic centimeter
Cd - cadmium
CGC - capillary gas chromatography
CI - Confidence Interval
Cl1 - monochloro-
Cl10 - decachloro-
Cl2 - dichloro-
Cl3 - trichloro-
Cl4 - tetrachloro-
Cl5 - pentachloro-
Cl6 - hexachloro-
Cl7 - heptachloro-
Cl8 - octachloro-
Cl9 - nonachloro-
cm - centimeter
Co - cobalt
Cr - chromium
Cu - copper
DBT - dibutyltin
DDD - Dichlordiphenyldichloroethane
DDE - Dichlordiphenyldichloroethylene
DDT - Dichlordiphenyltrichloroethane
df - degrees of freedom
dw - dry weight
ECD - electron capture detection
Fe - iron
FID - flame ionization detector
fw - fresh weight
fw - fresh weight
g - gram
GERG - Geochemical and Environmental Research Group
HCB - hexachlorobenzene
Hg - mercury

HpCDD - heptachlorodibenzo-p-dioxin
HpCDF - heptachlorodibenzofuran
HPLC - high performance liquid chromatography
HRGC - high resolution gas chromatography
HRMS - high resolution mass spectrometry
HxCDD - hexachlorodibenzo-p-dioxin
HxCDF - hexachlorodibenzofuran
ICP - inductively coupled plasma
IUPAC - International Union of Pure and Applied Chemists
K - potassium
LOD - limit of detection
lw - lipid weight
MBT - monobutyltin
MeHg - methyl mercury
Mg - magnesium
mg - milligram
ml - milliliter
mm - millimeter
Mn - manganese
Mo - molybdenum
MS - mass spectrometry
MSD - mass spectrometer detection
Na - sodium
nd - not detected
ng - nanogram
Ni - nickel
OC - organochlorine
OCDD - octachlorodibenzo-p-dioxin
OCDF - octachlorodibenzofuran
P - phosphorus
PAH - polynuclear aromatic hydrocarbon
Pb - lead
PBDE - polybrominated diphenyl ether
PCB - polychlorinated biphenyl
PCDD - polychlorinated dibenzo-p-dioxins
PCDF - polychlorinateddibenzofurans
PeCDD - pentachlorodibenzo-p-dioxin
PeCDF - pentachlorodibenzofuran
pg - picogram
ppb - parts per billion
ppm - parts per million
QA - quality assurance
QC - quality control
RI - Ratcliffe's Index
RPD - relative percent difference
S - sulfur

SCB - Southern California Bight
SD - Standard Deviation
Se - selenium
Si - silicon
SIM - selective ion mode
Sr - strontium
TBT - tributyltin
TCDD - tetrachlorodibenzo-p-dioxin
TCDF - tetrachlorodibenzofuran
TeBT - tetrabutyltin
TEF - toxicity equivalent factor
TEQ - toxic equivalent quotient
TERL - Trace Element Research Laboratory
Ti - titanium
µg - microgram
USDOI - U.S. Department of the Interior
USEPA - U.S. Environmental Protection Agency
USFWS - U.S. Fish and Wildlife Service
V - vanadium
WAI - West Anacapa Island
ww - wet weight
Zn - zinc

Units

µg/g = micrograms/gram or parts per million (ppm)
ng/g = nanograms/gram or parts per billion (ppb)
pg/g = picograms/gram or parts per trillion (pptr)

1 ppb = 0.001 ppm
1 pptr = 0.000001 ppm or 0.001 ppb
1 ppm = 1,000 ppb

1.0 INTRODUCTION

The California brown pelican (*Pelicanus occidentalus californicus*) was listed as federally endangered in 1970. Studies as early as 1969 documented severe reproductive impairments in nesting colonies on islands off the coast of southern California and northwestern Baja California that were subsequently attributed to organochlorine (OC) contaminants, including pesticides and polychlorinated biphenyls (PCBs; Anderson et al. 1975, 1977; Anderson and Gress 1983; Gress 1995). In the early 1970s, West Anacapa Island (WAI) was home to the last active pelican colony in the Southern California Bight (SCB). The WAI colony experienced nearly total failure, with 552 nest attempts and only one young fledged in 1970 (Gress 1970; Anderson et al. 1975). The low fledging rate reflected a low hatch rate due to eggshell thinning that led to crushed and/or broken eggs and subsequent abandonment of nests by adults (Gress 1970). With mean thicknesses of 0.29 millimeters (mm) and 0.40 mm respectively, the shells of both crushed and intact eggs (Risebrough 1972; Anderson et al. 1975) were substantially thinner than 0.572 mm observed with shells collected before 1943 and the extensive use of DDT (Anderson and Hickey 1970, 1975). Intact eggs from the WAI colony were analyzed for selected OC compounds and found to have high concentrations of dichlordiphenyltrichloroethane (DDT), most of which was as the breakdown product dichlordiphenyldichloroethylene (DDE), followed by polychlorinated biphenyls (PCBs) and to a lesser extent by dieldrin (Anderson et al. 1977). Geometric mean DDE levels reported for eggs from 1969 were 43,000 ng/g or parts per billion (ppb) fresh weight (fw; Anderson et al. 1977) or even higher (approximately 75,000 ng/g fw; Lamont et al. 1970), and as such were well above concentrations now established as thresholds for significant eggshell thinning and colony collapse in pelicans (>3,000 ng/g fw; Blus 1982, 1984, 1996; Risebrough 1972). In addition, concentrations of PCBs were sufficiently elevated to raise concern about the potential for adverse effects in embryos (typically reduced survival and malformations) and poor nest attentativeness by the adults (Anderson et al. 1977). The high concentrations of DDT and its metabolites, DDE and DDD in WAI pelican eggs were related to high concentrations in fish species collected near a local ocean outfall that discharged DDT and other contaminants from a manufacturing source nearby (MacGregor 1974).

The pelican colony on WAI has been monitored yearly (except 1995) for reproductive performance since the species was listed in 1970. In addition, concentrations of contaminants have been evaluated periodically in studies of failed eggs (Anderson et al. 1975, 1977), eggs collected opportunistically during colony surveys (Gress 1995), and during one study on viable eggs in 1992 (Gress 1995). Currently, data on measures of reproductive performance are available for nesting seasons up through 2006 in reports by Gress (1995, 2002), Gress et al. (2003), Gress and Harvey (2004) and Harvey and Gress (2008). Corresponding data on contaminant levels and eggshell thickness are available for nesting seasons from 1970 through 1992 (Gress 1995). Results of these activities demonstrated that multiple measures of productivity and eggshell thickness in the WAI colony improved, while concentrations of DDT and PCBs in eggs declined after ocean discharges containing waste from a local manufacturing source ceased in 1970, and the sale and use of DDT and PCBs in the United States were banned in the early to late 1970s

(Anderson et al. 1977; Anderson and Gress 1983; Gress and Anderson 1983; ATSDR 2000, 2002a).

Breeding effort (as number of nest attempts) improved since 1969, but with large annual fluctuations ranging in the hundreds during the middle 1970s, and in the thousands since 1979 (Anderson and Gress 1983; Gress and Harvey 2004). The number of young fledged per nest attempt at WAI increased from 0.002 in 1970 (1 fledgling / 552 nest attempts) up to 0.88 in 1975 (256 fledglings / 292 nest attempts), reflecting a reduction in the frequency of crushed eggs. Since 1976, the number of young fledged per nest has averaged approximately 0.65, with large annual fluctuations ranging from 0.18 - 1.24 (Gress and Harvey 2004). The improvements in productivity contributed to the decision by the USFWS to remove the brown pelican from the Federal Endangered Species List due to recovery in November 2009 (USFWS 2009).

Although improved, the long-term average for number young fledged per nest attempt at WAI remains below the mean of at least 1.0 observed in brown pelican colonies outside the SCB, including the Gulf of California where DDE occurred at much lower levels (Anderson and Gress 1983; Gress 2002). Eggshell thickness for pelicans from WAI also improved significantly since the 1970s. However, as of 1992, the mean eggshell thickness was still approximately 4.6% thinner than the mean for eggs prior to 1943 (Anderson and Hickey 1970; Gress 1995). Absent measurable impairments due to DDE-related eggshell thinning, it may be concluded that the annual fluctuations in productivity, and perhaps long-term trends in reproductive success are governed primarily by food supply and/or periodically by unusual events such as oil spills, toxic algal blooms, and human disturbance (Gress et al. 2003). However, long-term trends, and factors that govern them, are difficult to ascertain due to large annual fluctuations (Gress et al. 2003). One apparent long-term trend, the continuing low average for number of young fledged per nest, may be attributed to food supply (Anderson et al 1980, 1982; Anderson and Gress 1984). However, the occurrence of shell thinning may contribute as well. Gress (1995) provides the most current information on eggshell thickness, based on measurements in 1992. That shell thickness has not been measured since 1992 limits the ability to eliminate thinning as a potential contributor to low fledging rates observed as recently as 2006 (Gress and Harvey unpublished data; Harvey and Gress 2008).

Concentrations of DDE and other organochlorine compounds in WAI pelican eggs declined over the years for which there are records (1969 – 1992; Gress 1995). The decline in DDE concentrations was initially rapid (approximately 6-fold between 1969 and 1972; Anderson et al. 1977), followed by a steady but slow rate of decrease in years after 1972 (Anderson et al. 1977; Gress 1995). Concentrations of PCBs appeared also to decline at a steady but low rate throughout (Anderson et al. 1977). While there have been fluctuations, concentrations of DDE and PCBs appear to have changed little since the late 1980s (Gress 1995). By 1992, the mean concentration of DDE (2,300 ng/g fw), the only OC compound with data amenable to statistical analyses, was not significantly different from a mean of approximately 2,000 ng/g fw measured in 1980 (Gress 1995). Dieldrin, chlordanes, hexachlorcyclohexanes and hexachlorbenzene were also detected in the eggs of pelicans from WAI, but at concentrations that were below levels of concern for

reproductive effects (Gress 1995). Based on the most recent data from 1992, the mean concentration of DDE in pelican eggs was below levels of concern, but there continue to be individuals, with DDE concentrations that exceed thresholds for significant eggshell thinning. The continued presence of DDE at concentrations that may exert effects on individuals if not the colony as a whole, suggest that contaminants, while possibly secondary to factors such as food supply, cannot yet be completely ruled out as a limiting factor in the low fledging rates and eggshell thinning observed in the WAI colony (Gress 1995).

Prior to this study, contaminant levels had not been measured in WAI pelican eggs since 1992 and whether concentrations had changed since then is unknown. The compounds detected in eggs collected up through 1992 have not been manufactured and/or extensively used in the United States since the mid-1970s to mid-1980s, depending on the substance. Because uses have been banned or curtailed, many of the organochlorine compounds previously measured in pelican eggs are considered legacy pollutants (i.e., no longer in use, but still present in the environment). Concentrations of legacy pollutants in pelican eggs are expected to decline over time. However, rates of decline may be small and hard to detect due to the high persistence of the OCs in environmental media, and limitations posed by sampling and analytical protocols for different investigations. In addition, there is a potential for exposure to some OC compounds that are still in use in countries outside the United States, some that are still produced in small quantities within the U.S. as industrial byproducts or waste, and some that are persistent breakdown products of less persistent current use parent compounds.

Pelicans are at risk of exposure to many pollutants that tend to be persistent and have a high potential for bioaccumulation and biomagnifications in marine food webs. Pelicans nesting off the coast of southern California are dependent on the northern anchovy (*Engralus mordax*) and Pacific sardines (*Sardinops sagax*) for food (Anderson and Gress 1983; Anderson et al 1980, 1982; Harvey and Gress 2008). As a result, pelicans like other piscivorous seabirds are upper trophic level species in marine food webs (e.g., Sydeman et al. 1997) and are at high risk of exposure to unsafe levels of bioaccumulative contaminants in marine environments. In addition to legacy organochlorines, pelicans and other seabirds may be exposed to newer use substances that also have a high potential for uptake and accumulation in marine food webs. Notable among these are the polybrominated diphenyl ethers (PBDEs), which are used as flame retardants in common commercial products. The PBDEs are highly bioaccumulative and concentrations measured from fish to human adipose tissue have been increasing rapidly over time (ATSDR 2004). There are no known natural sources of PBDEs, so releases of these compounds are expected to be greatest in areas where they are extensively used, which includes areas with dense residential and industrial development. Land use along the coast of southern California is such that releases of PBDEs into coastal waters may potentially be significant. PBDEs are structurally similar to PCBs, and they have been shown to act additively in neurologic (behavior) and thyroid hormone function tests with small mammals (ATSDR 2004, McDonald 2004) and avian species (Fernie et al. 2005). PBDEs have also been associated with eggshell thinning in birds (Fernie et al. 2009). Because of their increasing prevalence in the environment, the potential for significant

releases into the local environment, the potential to act additively with PCBs and cause eggshell thinning, PBDEs constitute an important class of contaminants to consider for California brown pelicans nesting off the coast of southern California.

This study was conducted to reduce uncertainty about current levels of contaminants in eggs of California brown pelicans nesting on WAI, and to evaluate temporal trends and the potential role of contaminants as a limiting factor for productivity in the WAI colony. Specific objectives of this study were:

1. To characterize and evaluate recent changes, if any, in the condition of brown pelican eggs from WAI;

2. To quantify and evaluate recent temporal changes, if any, of legacy organochlorine compounds in California brown pelican eggs;

3. To quantify and evaluate recent temporal changes, if any, of bioaccumulative contaminants that were not quantified in the past;

4. Identify potential recovery data points as benchmark concentrations for contaminants in California brown pelican eggs; and,

5. Evaluate if contaminants are currently a stressor or threat for California brown pelicans.

2.0 METHODS

2.1 Sample collection and processing

Contaminant levels were measured in viable pelican eggs collected by F.Gress from nests on WAI (Figure 1) during surveys in 1993 and 2005. Eggs were collected and processed using methods described in Gress (1995) for another study conducted in 1992.

A total of 25 eggs were collected in 1993, of which 15 were randomly selected for this study. An additional 15 eggs were collected in 2005. To minimize disturbance to the colony, eggs were taken from nests in close proximity to one another. One egg was collected per nest. After collection, all nests containing eggs were covered lightly with vegetation to help prevent predation by western gulls (*Larus occidentalis*). When collected, eggs were placed in plastic Whirl-Pak bags, labeled and placed in padded egg case for transport back to the Davis, California, location of California Institute of Environmental Studies. Eggs were weighed, measured, and processed in a laboratory at University of California, Davis. Intact eggs were frozen, then slightly thawed to facilitate removal of contents. Partially thawed eggs were first measured for dimensions, weight, and volume. Contents were subsequently processed using standard methods. Briefly, all eggs were measured for length (mm), breadth (mm) and weight (g). Because eggs were intact, it was also possible to measure displacement volume (cc). Eggs were opened by scoring around the girth using hexane-rinsed scalpels. Contents were transferred to

hexane-rinsed jars and evaluated for status with regard to fertility and stage of development if an embryo was present. Embryos were also evaluated for evidence of gross abnormalities, such as malformations and malpositioning within the shell. Egg contents were placed in a freezer for storage until arrangements for chemical analyses could be made. Once funding became available, eggs were packed and shipped on dry ice to laboratory under contract with USFWS for chemical analyses (Section 2.2 below). The empty shells and all shell chips were rinsed with water and placed in small paper bags to dry at room temperature for at least one week. Dried shells were later weighed and their thickness measured. The thickness of each shell (with membranes) was measured using a micrometer, to the nearest 0.01 mm at six or more points around the girth. Results are reported as the mean of the measurements for each egg.

Figure 1. Location of West Anacapa Island, Southern California Bight.

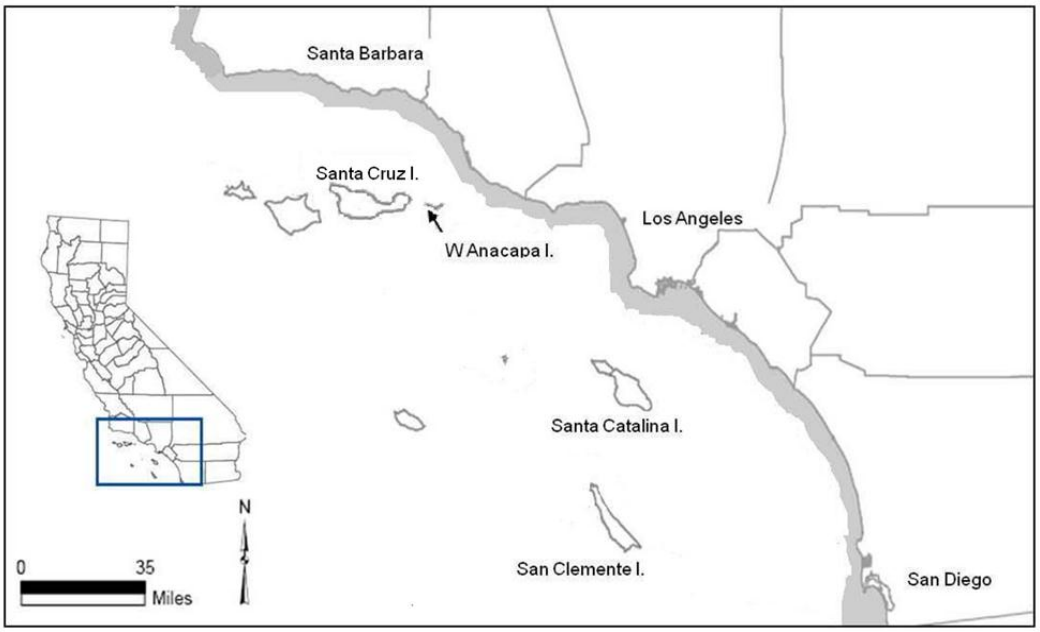


Figure modified from CH2M Hill (2003).

Another common value used for evidence of shell thinning is Ratcliffe's Index (RI) as described by Burnham et al. (1984) and used previously for pelican eggs by Anderson and Hickey (1970). The RI for each egg was computed as:

RI = dry weight of the shell (mg) / [shell length (mm) x shell breadth (mm)], which is equivalent to

RI = 10 x dry weight of the shell (g) / [length (cm) x breadth (cm)] from Anderson and Hickey (1970).

2.2 Chemical analyses

A. Target analytes

Chemical analyses were conducted with funding from USFWS, by laboratories under contract to the USFWS Analytical Control Facility (ACF) at Shepherdstown, West Virginia. A total of 30 eggs (15 from each collection year) were submitted for chemical analyses. These included all 15 collected in 2005, and 15 that were randomly selected from among the 25 collected in 1993. Samples were analyzed for a variety of organic contaminants by Geochemical and Environmental Research Group (GERG), College Station, Texas, who also submitted splits to Trace Element Research Laboratory (TERL), College Station, Texas to be analyzed for metals, metalloids (B, Si, Se, As) and non-metal elements (P, S).

All samples were analyzed for percent moisture, lipid content, OC pesticides, PCBs, polychlorinated dibenzo-p-dioxins and furans (PCDDS/PCDFs), PBDEs, organotin compounds, metals and methylmercury. A randomly selected subset of 15 eggs (eight from 2005 and seven from 1993) was analyzed for polynuclear aromatic hydrocarbons (PAHs).

The target OC pesticides include aldrin; α-, β-, γ- and δ-benzene hexachloride (BHC); α- and γ-chlordane; *cis*- and *trans*-nonachlor; dieldrin; endrin; endosulfan II; hexachlorobenzene (HCB); heptachlor; heptachlor epoxide; mirex; o,p′-DDD; o,p′-DDE; o,p′-DDT; oxychlordane; p,p′-DDD; p,p′-DDE; p,p′-DDT; pentachloro anisole; toxaphene; 1,2,3,4- and 1,2,4,5-tetrachlorobenzenes; and, total PCBs (as Aroclor). Detection limits for total PCBs and toxaphene were 4.0 ppb wet weight (ww). The detection limit for all others was 0.02 ppb ww.

Samples were analyzed for 93 PCB congeners that were quantified individually (70 congeners) or in combination with other co-eluting congeners (23 congeners plus co-elutes). The target PCB congeners, as designated by their International Union of Pure and Applied Chemists (IUPAC) numbers, included ten planar and co-planar PCBs (PCB congeners 77, 81, 105, 114, 118, 126, 157, 167, 169, and 189) specifically recognized for their dioxin-like toxicity (Van den Berg et al. 1998). Analytes also included congeners from all homolog classes (PCB congeners 1 through 209), and those most frequently measured in aquatic biota (95, 101, 110, 118, 138, 153, and 180; ATSDR 2000). The detection limit for individual congeners was 0.04 ppb ww. PCBs were also quantified according to homolog classes (Cl1, CL2, Cl3, Cl4, Cl5, Cl6, Cl7, Cl8, Cl9, and Cl10), with a reported detection limit of 4.0 ppb ww for each homolog class.

Samples were analyzed for 17 PCDD and PCDF congeners with chlorines occupying the 2,3,7, and 8 positions. These include 2,3,7,8-TCDD (hereby referred to as TCDD), 2,3,7,8-TCDF (hereby referred to as TCDF), and penta-, hexa-, hepta- and octa-CDDs/CDFs. Detection limits for TCDD and TCDF were 0.0095 ppb ww. The detection limits for OctaCDD (OCDD) and Octa-CDF (OCDF) were 0.0945 ppb ww, and the detection limit for all other congeners was 0.0473 ppb ww.

Samples were analyzed for 38 individual PBDE congeners and total PBDEs. The target PBDE congeners, included representatives of the mono-, di-, tri-, tetra-, penta-, hexa- and heptabromo homolog classes. Mean detection limits were 0.46 ppb ww for the mono-, di, tri- and tetra-BDEs, 0.69 ppb ww for the penta-BDEs, 0.92 ppb ww for hexa-BDEs, 1.15 ppb ww for hepta BDEs and 9.18 ppb ww for total BDEs.

All samples were analyzed for monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT and tetrabutyltin (TeBT). The detection limit for butyltins was 10 ppb ww.

A subset of 15 egg samples was analyzed for 44 individual PAH compounds including 19 parent compounds (naphthalene, biphenyl, acenaphthalene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, perylene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, and dibenzothiophene), and 24 alkylated homologs. The mean detection limit was 23.4 ppb ww for each of the individual PAH compounds.

All samples were analyzed for silver (Ag), aluminum (Al), arsenic (As), boron (B), barium (Ba), beryllium (Be), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), methylmercury (MeHg), potassium (K), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), phosphorus (P), lead (Pb), sulfur (S), selenium (Se), silicon (Si), strontium (Sr), titanium (Ti), vanadium (V), and zinc (Zn). Detection limits were variable, ranging from 0.0003 ppm ww for mercury to 1.0 ppm ww for silicon and potassium. Because they were so variable, detection limits for the target inorganic analytes are provided with results.

B. Chemical extraction and analyses

Details of methods used for extraction, cleanup and quantification of target analytes are described in reports from the analytical laboratories and can be obtained from the ACF web site at the following web address:

http://www.fws.gov/chemistry/acf_analytical_methods.htm

Briefly, for OC pesticides, PCBs, PAHs, and PBDEs, tissue samples were homogenized, with added surrogate standards, sodium sulfate and methylene chloride. The tissue extracts were purified by silica/alumina column chromatography to isolate the aliphatic and PAH/pesticide/PCB fractions. The PAH/pesticide/PCB fraction was further purified by high-performance liquid chromatography (HPLC) in order to remove interfering lipids.

Quantification was performed by capillary gas chromatography (CGC) with an electron capture detector (ECD) for pesticides and PCBs, and a mass spectrometer detector (MSD) in the Selective Ion Monitoring (SIM) mode for aromatic hydrocarbons. For analytes that are known to co-elute with other analytes (e.g., Endosulfan I and PCB

congeners 114 and 157), samples were analyzed by CGC with a mass spectrometer detector in the SIM mode. Concentrations of PBDEs were also quantified using CGC with a mass spectrometer detector in the SIM mode.

Extraction and analyses for PCDDS and PCDFs entailed spiking with a solution containing each of fifteen isotopically ($^{13}C_{12}$) labeled PCDDs/PCDFs, followed by filtration to separate solid phase and aqueous phase sample, and solvent extraction. Following extraction and a solvent exchange step, the extracts were cleaned up by column chromatography on alumina over silica gel, and AX-21 activated carbon on silica. Concentrations of PCDDs and PCDFs were quantified using HRGC/HRMS in SIM mode.

Concentrations of butyltins were determined using methods specific to tissue samples. Aliquots of homogenized sample were extracted using a Tissumizer with tropolone in methylene chloride and sodium sulfate as a drying agent. Extracts were combined, concentrated and methylene chloride replaced by hexane. The samples were hexylated using hexylmagnesium bromide, followed by neutralization, removal of the organic fraction and re-extraction of the aqueous fraction. Organic extracts were combined, concentrated and transferred to an alumina/silica column for cleanup. Concentrations of organotins were quantified using atomic absorption spectrophotometer (AAS) with flame ionization detector (FID).

For metals, tissue samples were wet digested with nitric acid and converted into acidic digest solutions for analysis by various atomic spectroscopy methods. When possible, tissue was freeze dried and homogenized prior to acid extraction. Aliquots of digested sample were analyzed for most of the target metals using inductively coupled plasma (ICP) optical emission spectroscopy.

Analyses for arsenic, cadmium, lead and selenium entailed the use of ICP in combination with mass spectrometry (ICP-MS).

Concentrations of total mercury were quantified using combustion in a stream of oxygen followed by trapping on a gold column. Electrothermal heating was used to release mercury from the column, which was then quantified using AAS.

Samples were analyzed for methyl mercury using ethylation with sodium tetraethyl borate, followed by trapping on a Tenax column, then separation on an isothermal gas chromatography column. Following pyrolysis of separated species, mercury was quantified using atomic fluorescence spectroscopy.

C. QA/QC

For quality assurance and quality control (QA/QC), chemical analyses were performed using methods and control procedures required under the contract with the USFWS's ACF. Once available, results were reviewed at ACF to determine that QA/QC procedures had been followed and conditions specified in the contract were satisfied.

Anomalies identified during the QA/QC process are noted in the QA/QC report provided by ACF.

Analyses for inorganic analytes met QA/QC requirements. Analyses for a number of the organic analytes were flagged for a variety of anomalies. Some of the target analytes with reported QA/QC anomalies were not detected in any samples, and therefore were not considered further. Blank, precision and recovery anomalies for detected target analytes are summarized as follows:

1. Dibutyltin (DBT), monobutyltin (MBT) and PCB# 175 were detected in blanks. The reported concentrations for DBT and MBT were less than 10-times the background equivalent concentration in blanks, and therefore results for DBT and MBT are considered non-detects. Reported concentrations for PCB# 175 were high enough to be considered valid detections.

2. The percent recovery of internal standards was below 80% for α-chlordane (64% recovery), PCB# 66 (53% recovery) and o,p'-DDT (47% recovery). Concentrations of these analytes may be underestimated by reported values. Although non-detects are not considered in detail, the failure to detect a number of individual PAHs (37% to 71% recoveries), 2,3,7,8-TCDD (32% recovery) and 1,2,3,4,7,8-HxCDD (55% recovery) may be due in part to low recovery rates.

3. The percent recovery of internal standards was above 120% for 2-methylnaphthalene, a number of PBDE congeners (BDE# 28, 66, 99, 100, 153 and 154), two PCB congeners (PCB# 118 and 209), endrin, and 2,3,7,8-TCDF. For all but three of these, the recovery was between 130% and 167%. Even higher recovery rates were obtained with 2-methylnaphthalene (195% recovery), PCB# 118 (185% recovery) and 2,3,7,8-TCDF (269% recovery). Concentrations of these analytes, especially the last three may be overestimated by reported values.

4. The relative percent difference (RPD) between duplicates was greater than 17% for a number of analytes. The RPD was between 30% and 60% for α-chlordane, heptachlor epoxide, o,p'-DDE, o,p'-DDT, and heptachlor. The RPD was 74% for BDE# 99, and the RPD was much higher for naphthalene (179%) and PCB# 197 (187%). The RPD for DBT, which is considered not-detected due to blank anomalies, was also very high. It is recommended in the QA/QC report that positive results of these analytes be considered estimates. The high RPDs for all but endrin were observed in only one of two samples for which duplicates were taken. Consequently, uncertainty about reported values for all but endrin is limited.

2.3 Data analysis

Results of chemical analyses are presented as fresh weight (fw)-based concentrations, which entail adjustments of analytical results for moisture loss that can occur with time

between when the egg was laid and when it was collected. To obtain fw-based values, wet weight-based contaminant levels reported by the contract laboratory were adjusted according to methods by Stickel et al. (1973), using volume and weight measurements obtained for each egg. All of the eggs were intact and all but one had embryos at various stages. Consequently moisture loss from samples was limited and adjustment factors were all greater than 0.92, making fresh weight-based concentrations near if not equal to the wet weight-based concentrations for all eggs.

For some comparisons with literature, fw-based contaminant levels may be converted to dry weight (dw)-based concentrations as follows:

$$\text{Dry weight concentration} = \text{fresh weight concentration} \times [1 - (0.01 \times \% \text{ moisture})]^{-1}$$

This conversion assumes that the fw and ww-based contaminant levels are essentially equal, which is the case in this study. Percent moisture values are provided in results tables to enable the conversion, if desired.

Concentrations of selected organic contaminants were also normalized for the fraction of lipid (% lipid / 100), to enable comparisons with results from studies that report results on a gram-lipid basis (e.g., She et al. 2008).

Results of analyses for inorganic contaminants are all reported as µg/g, or ppm fw. Concentrations of organic analytes, which tended to be much lower than those of inorganic analytes, are reported as ng/g or ppb fw. Lipid normalized results were reported as ng/g-lipid.

A. Computing concentrations of mixtures

The PCBs, PBDEs, DDT and metabolites, chlordanes, and BHCs are chemical classes for which concentrations of multiple individual compounds were measured. While it was desirable to know the measured concentrations of the individual components, it was also desirable to have an estimate of the concentrations of the mixtures as a whole. The concentration of total PCBs was determined three ways: 1) as the sum of the detected aroclors (as reported by the laboratory); 2) the sum of the homologs, using ½ the detection limit as a surrogate for non-detects; and, 3) the sum of the congeners using ½ the detection limit as a surrogate for non-detects. Concentrations of total DDT, chlordanes, and BHCs were also computed as the sums of the concentrations of individual constituents, using ½ the detection limit as a surrogate for non-detects.

The total DDT concentration is the sum of the concentrations of six isomers (o,p- and p,p' DDT, o,p- and p,p' DDE, and o,p- and p,p' DDD). The total chlordane concentration is the sum of the concentrations for major constituents in technical grade chlordane (α- and γ-chlordane, *cis*- and *trans*-nonachlor) and the primary metabolite oxychlordane (as applied by USEPA 1992). The total BHC concentration was computed as the sum of the concentrations of four isomers (α-, β-, γ- and δ-BHC). Because only a few of the 38 PBDE congeners were detected, total PBDE concentrations were computed as the sum of

the detected congeners (non-detects were essentially assigned a value of zero). The PAHs are often evaluated by summing the concentrations of the individual constituents. This was not done for this study because only two constituents were detected in two samples, and because of uncertainty with the QA/QC, the PAHs were considered to be not detected.

Toxic equivalent concentrations (TEQs) were computed for mixtures of dioxins, furans and dioxin-like PCB congeners using dioxin toxicity equivalent factors (TEFs) for avian species from Van den Berg et al. (1998).

B. Statistical analyses

Contaminant levels measured in pelican eggs from 1993 were compared with levels measured in eggs from 2005 for evidence of changes over time. Data on organic contaminants were natural-log transformed to better meet the assumptions of standard parametric statistical tests and to normalize residuals. Data on inorganic analytes were not amenable to standard parametric tests, even when transformed. Consequently, for inorganics, statistical comparisons were conducted using non-parametric tests with untransformed data. Statistical analyses were run only for those analytes detected in more than ½ of the samples for each of the two sample years.

A two-sample student's t test was used to evaluate differences between Ln-transformed concentrations of organic analytes in eggs from 1993 with those in eggs from 2005 (Sokal and Rohlf, 1981). Differences were considered significant at $p<0.05$ (28 df, two-tailed test). Values of "p" were computed using the Microsoft EXCEL estimator.

Two-sample comparisons for inorganic analytes were carried out using the Mann-Whitney U test for significance ($p<0.05$; Zar 1999).

3.0 RESULTS AND DISCUSSION

3.1 Eggs and eggshell characteristics

All of the eggs collected for this investigation were in good condition; shells had no cracks, no deposits, or excessive soiling. With the exception of one infertile egg, eggs collected in 1993 contained embryos at various stages of development (Table 1). All of the eggs collected in 2005 had late-stage embryos. No signs of abnormalities were noted.

Eggs collected in 1993 had similar dimensions and were the same overall size (as volume), as eggs collected in 2005. While dimensions showed no change, shell weights increased between 1993 and 2005, a change that also reflects an increase in shell thickness (Table 2).

Table 1. Basic features of brown pelican eggs collected from W. Anacapa Island, California in 1993 and 2005.

		1993	2005
developmental stage	number infertile	1	0
	number fresh	3	0
	number early-stage	3	0
	number mid-stage	3	0
	number late-stage	5	15
shell breadth (mm)	mean (95% CI)	50.7 (0.70)	50.82 (1.00)
shell length (mm)	mean (95% CI)	79.53 (1.84)	77.71 (1.61)
egg volume (mm)	mean (95% CI)	103.0 (4.05)	102.1 (4.81)

The mean shell thickness and shell weight of eggs collected in 1993 are approximately 6% thinner than the mean thickness and weight observed by Anderson and Hickey (1970) with pelican eggshells collected before 1943 (Table 2). The percent thinning observed with eggshells from 1993 is slightly greater than the approximately 5% thinning noted by Gress (1995) for eggs collected in 1992. The mean thickness of shells from 2005 is significantly greater than the mean thickness observed in 1993, and is not significantly different from mean thickness reported for shells of eggs collected before 1943 (Table 2 and Figure 2).

The apparent temporal differences in eggshell thickness may reflect: (1) changes in concentrations of DDE and other contaminants that affect eggshell thickness; (2) differences in the methods and / or equipment used for measuring thickness; and, (3) natural variation relating to factors such as the egg's stage of development, maternal nutritional status, and shifts in the gene pool among others (Klaas et al. 1974). With respect to the last, although not significant, the mean shell thickness in 2005 was 102 % of the mean thickness in pre-1943 eggs and may reflect selection over the intervening years for birds that produce eggs with thicker shells. Other than being crush-resistant, the physiological implications of thicker shells for the developing pelican embryos, such as differences in oxygen exchange are not known.

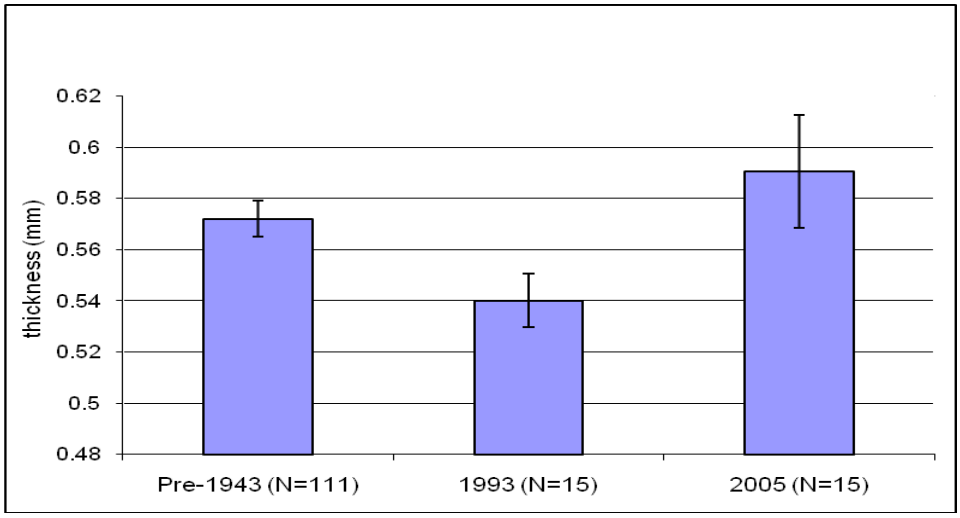
With regard to potential measurement artifacts, the thickness values reported by Anderson and Hickey (1970) were measured using the same kind of micrometer and same methods as were used for this study (1993 and 2005). In addition, measurements were taken by a single investigator for this study where the greatest differences in shell thickness were observed. The differences observed with shell thickness were also observed with shell weight and Ratcliffe's Index (Table 2), both of which entail measurements with devices (balances and calipers) other than micrometers. Consequently, the observed temporal trend in shell thickness does not appear to be due measurement artifacts.

Table 2. Comparison of eggshell measurements for brown pelican eggs collected from W. Anacapa Island, California in 1993 and 2005, with features of pre-1943 shells from WAI.*

	Thickness (mm)	
	mean (range)	95% CI
Pre-1943 (N=111)*	0.572	0.007
1993 (N=15)	0.540 (0.512 - 0.572)	0.010
2005 (N=15)	0.591 (0.520 - 0.663)	0.022
	Shell weight (g)	
	mean (range)	95% CI
Pre-1943 (N=85)*	10.59	0.24
1993 (N=15)	9.90 (8.60 - 11.0)	0.34
2005 (N=15)	10.42 (8.64 - 11.4)	0.44
	Ratcliffe's Index (mg / mm^2)	
	mean (range)	95% CI
Pre-1943 (N=44)*	2.71	0.04
1993 (N=15)	2.45 (2.33 - 2.72)	0.06
2005 (N=15)	2.64 (2.34 - 2.89)	0.08

* Pre-1943 from Anderson and Hickey 1970 and Anderson et al. 1975. 1993 and 2005 from this study.

Figure 2. Shell thickness (mean ± 95% CI) of brown pelican eggs collected from W. Anacapa Island, California prior to 1943 and in 1993 and 2005*.

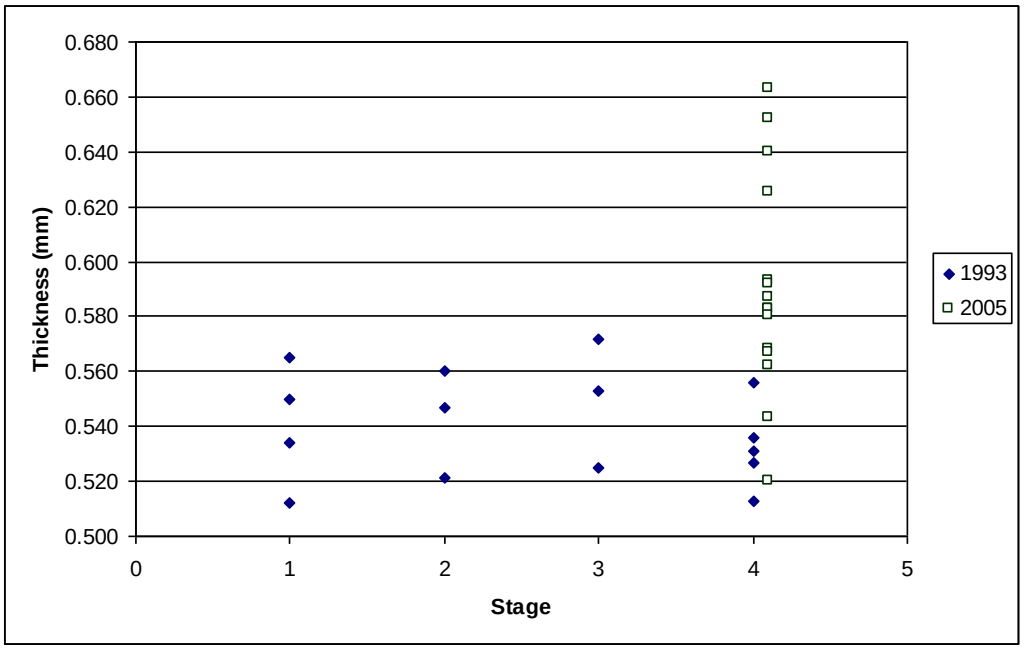


* Pre-1943 from Anderson and Hickey 1970 and Anderson et al. 1975. 1993 and 2005 from this study.

Some differences in shell thickness have been related to the developmental stage of the embryo (Bunck et al. 1985) that reflect changing demands for calcium by the developing embryo (Klaas et al. 1974). In this case, shells of eggs with late-stage embryos are

expected to be thinner than shells of eggs with early stage embryos. All of the eggs collected in 2005 had late stage embryos whereas eggs collected in 1993 included very early to mid-stage embryos (Table 1). Data from 1993 suggests that shells of some late stage embryos may be slightly thinner than shells of earlier stage embryos. However the difference is not significant, and if thickness is plotted as a function of egg stage (Figure 3) the stage of embryo development does not appear to explain why eggs collected in 2005 had thicker shells than eggs collected in 1993.

Figure 3. Shell thickness as a function of developmental stage of brown pelican eggs collected from W. Anacapa Island, California in 1993 and 2005.



Stages: 1 = fresh or unfertilized, 2 = early, 3 = mid, and 4 = late.

Eggshell thickness for pelicans from WAI improved significantly since 1969 when the mean thickness for intact eggs was 0.402 mm (Anderson et al. 1977), which is approximately 30% thinner than shells of eggs collected before 1943 (Anderson and Hickey 1970). The reduction was even greater (approximately 50%) for fragments collected in 1969, which had a mean thickness of 0.287 mm (Risebrough 1972). The amount of thinning declined to approximately 16% by 1974 (Anderson et al. 1977). Some thinning was still evident by 1993, when shells of viable eggs from the WAI colony were, on average, 6% thinner than shells of pelican eggs collected before 1943 (Gress 1995; Anderson and Hickey 1970). This is below the critical value of 18% eggshell thinning associated with population declines (Blus 1984), and may be within the range observed with eggs from colonies with no measurable impact on nest success (Blus 1984). Whether even a small percentage of thinning is sufficient to result in subtle effects, such as an occasional cracked but not crushed eggshell, is not known. However, the concern about a small percentage of thinning may be moot because by 2005, the percent thinning, on average was reduced to 0%. Therefore, it appears that as of 2005,

eggshell thinning is no longer a potential limiting factor for reproductive success of brown pelicans on WAI.

Shells of four eggs collected in 2005 had thicknesses greater than 0.620 mm (Figure 3), and as such are unusually thick compared with shells collected before 1943 (Table 2). Whether this reflects natural variation or an ongoing trend over which there has been selection for individuals that produce eggs with thicker shells is unknown. Because shell thickness may exhibit some natural variation (Klass et al 1974; Anderson and Hickey 1970), additional sampling is recommended to confirm that thicknesses observed in 2005 represent more than natural variation, and instead represent a permanent recovery to pre-1943 conditions.

3.2 Organic contaminants

Napthalene and methyl-naphthalenes were the only PAH compounds detected in pelican eggs. Naphthalene was detected in three eggs from 1993, but detections are believed to represent interferences that also affected recovery of internal standards. Methyl-naphthalenes were detected in a fourth egg at very low concentrations. Given the uncertainty about reported concentrations and absent the occurrence of other PAHs, we conclude that the few positive values reported for PAHs are analytical anomalies and the PAHs were not detected in any of the pelican eggs.

Butyltin compounds were either not detected or are considered non-detects due to QA/QC anomalies. Tetrabutyltin and tributyltin were not detected in any samples. Monobutyltin and dibutyltin were detected in most samples. However, percent recoveries of internal standards for MBT and TBT were high, and both were detected in procedural blanks. None of the reported concentrations for MBT or TBT were high enough compared with the blanks to be considered detects.

Nearly all of the organochlorine analytes were present at detectable levels in pelican egg samples. The exceptions are aldrin, δ-BHC and toxaphene which were not detected in any samples, endosulfan II which was detected in only 3 samples, and 1,2,4,5-tetrachlorbenzene was detected in only 10 samples. All others were detected in more than 20 samples, and most of the OCs were detected in all 30 samples (Table 3).

All of the DDT isomers were detected in eggs from both 1993 and 2005. By far, the predominant isomer was p,p'-DDE which constituted more than 80% of the total in all eggs and was more than 95% of the total on average (Table 3). The relative contribution of DDE to total DDT reflects exposure to breakdown product (DDE), rather than parent compound (DDT), and therefore the DDTs measured in pelican eggs were not from an encounter with recently applied DDT.

The chlordanes detected in pelican eggs were primarily nonachlors, which averaged more than 70% of the total, followed by the metabolite, oxychlordane which averaged approximately 10% of the total. Of the BHCs, β-BHC was the predominant isomer (69% to 88% of the total), followed by α-BHC. γ-BHC (Lindane) was detected, but at much

lower concentrations than β-BHC. Of the cyclodienes, dieldrin was detected in all samples, whereas aldrin was not detected in any, most likely because it is readily converted to dieldrin once released into the environment (ATSDR 2002b). The occurrences, and dominance of specific isomers/metabolites of organochlorine compounds in the pelican eggs collected in 1993 and 2005 from WAI are similar to what has been reported for eggs collected within the same timeframe of other seabird species that nest along the Pacific coast of Canada (Harris et al. 2005) and San Diego Bay (Zeeman et al. 2008).

The overall mean organic contaminant load in pelican eggs from WAI declined from nearly 2,800 ng/g fw in 1993 to approximately 1,500 ng/g fw in 2005. In both years, the total was clearly dominated by DDTs and PCBs. The PBDEs contributed approximately 4% in 1993 and 8.5% in 2005, chlordanes contributed approximately 2% to the total, and the remaining OC compounds contributed even less (Figure 4). In absolute terms, concentrations of DDTs and PCBs each reached levels greater than 1,000 ng/g fw and concentrations of chlordanes and PBDEs reached levels between 100 ng/g fw and 1,000 ng/g fw. In comparison, concentrations of aldrin/dieldrin, BHC and HCB were all below 100 ng/g fw and concentrations of the remaining organic analytes were below 10 ng/g fw.

Figure 4. Percent contributions of DDT, PCBs, chlordanes, other organochlorine pesticides and PBDEs to the total organic contaminant concentration in brown pelican eggs collected from W. Anacapa Island, California in 1993 and 2005.

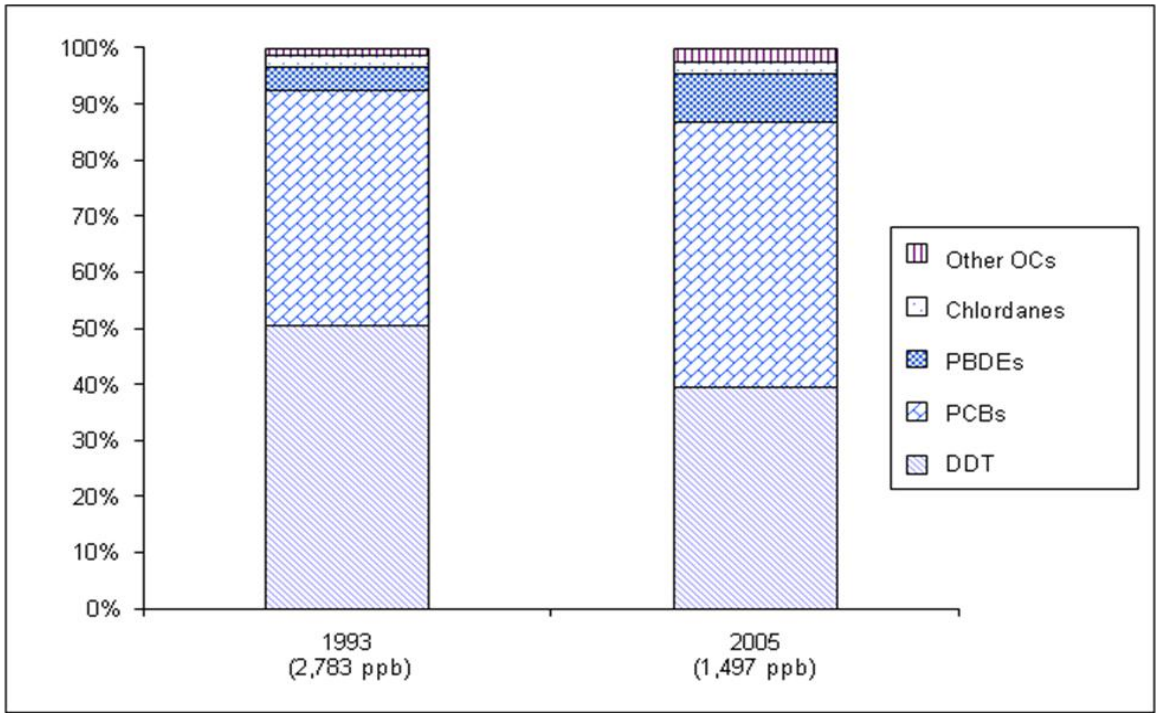


Table 3. Summary of organochlorine and PBDE concentrations, as ng/g fresh weight (ppb fw) measured in brown pelican eggs collected from W. Anacapa Island, California in 1993 (N=15) and 2005 (N=15). Changes between 1993 and 2005 are noted, and considered not significant for p>0.05.

	1993				2005					
Analyte	geomean	(Range)	± 1 SD	detects (N=15)	geomean	(Range)	± 1 SD	detects (N=15)	change ('93 →'05)	p (student's t)
% Lipid	2.28	(1.60-3.04)			2.88	(2.14-4.28)				
% Moisture	83.1	(81.8-84.4)			83.7	(81.8-86.2)				
Aldrin/Dieldrin	15.8	(6.56-42.6)	9.3-27	15	13.2	(2.62-23.4)	7.7-22	15	→	0.1966
∑ BHC (HCH)	11.2	(6.02-24.4)	7.9-16	15	9.68	(4.43-25.4)	6.3-15	15	→	0.1585
∑Chlordanes	56.9	(18.9-168)	30-109	15	30.0	(11.9-66.2)	19-47	15	↓	0.0001
Heptachlor	0.31	(<0.142-5.55)	0.1-1.3	8	0.766	(0.054-2.79)	0.2-2.7	13	↑	0.0160
Heptachlor epoxide	1.55	(<0.406-8.78)	0.6-3.9	14	0.900	(<0.192-3.94)	0.3-3.1	12	↓	0.0642
p,p'-DDE	1,319	(454-12,722)	519-3,351	15	532	(184-1,628)	284-1,015	15	↓	0.0002
∑ DDT	1,402	(484-12,982)	563-3,494	15	566	(201-1,678)	303-1,045	15	↓	0.0006
Endosulfan II	<0.18			0	0.193	(<0.108-3.40)		3		
Endrin	3.56	(2.35-9.52)	2.4-5.2	15	3.87	(1.87-8.95)	2.3-6.5	15	→	0.4979
HCB	4.38	(2.63-9.54)	2.9-6.6	15	6.39	(3.69-16.0)	4.3-9.6	15	↑	0.0012
Mirex	2.32	(0.576-7.00)	1.2-4.4	15	0.914	(<0.208-7.76)	0.3-2.6	14	↓	0.0002
∑PCBs (aroclor)	1,168	(377-3,161)	595-2,294	15	710	(362-1,517)	424-1,188	15	↓	0.0033
Pentachloroanisole	0.25	(<0.166-0.854)	0.1-0.5	12	0.405	(0.204-1.05)	0.3-0.7	15	↑	0.0029
Tetrachlorobenzenes	0.42	(<0.262-1.85)	0.2-1.0	10	0.783	{0.253-2.00)	0.5-1.3	15	↑	0.0019
Toxaphene	<3.5			0	<3.8			0		
∑ PBDEs	116	(29.8-607)	53-252	15	132	(61.5-517)	68-255	15	→	0.4983
Total TEQ	0.152	(0.058-0.510)	0.1-0.3	15	0.101	(0.048-0.203)	0.1-0.2	15	↓	0.0100
Relative Contributions										
p,p'-DDE/∑ DDT	0.94	(0.81-0.99)			0.95	(0.91-0.98)				
Beta BHC/∑ BHC	0.78	(0.72-0.88)			0.82	(0.69-0.86)				
nonachlors/∑Chlordanes	0.75	(0.71-0.79)			0.72	(0.48-0.83)				
oxychlordane/∑Chlordanes	0.10	(0.06-0.20)			0.11	(0.09-0.20)				
∑ DDT/∑PCBs	1.20	(0.27-4.20)			0.80	(0.27-1.47)			→	0.0159

A. DDT / DDE

The DDT concentrations measured in brown pelican eggs collected from WAI in 1993 and 2005 are much lower than concentrations measured in eggs collected from pelicans on WAI 35 - 40 years ago. Anderson et al. (1977) summarized changes in lipid-based concentrations of DDE and PCBs observed with WAI pelican eggs collected over years between 1969 and 1975. Lipid-based concentrations of DDT, PCBs and other organochlorines measured in pelican eggs collected for this study (1993 and 2005) are provided in Table 4 for comparison. Data reviewed by Anderson et al. (1977) demonstrate a substantial initial drop in mean DDE concentrations from approximately 850,000 ng/g lw in 1969 to approximately 175,000 ng/g lw in 1973, followed by a slower decline to 113,000 ng/g lw in 1975. The initial 6-fold drop is attributed to the cessation in 1970 of releases of wastewater carrying DDT from an industrial source into the Pacific Ocean off the coast of the Palos Verde Peninsula near Los Angeles (Anderson et al. 1975; MacGregor 1974).

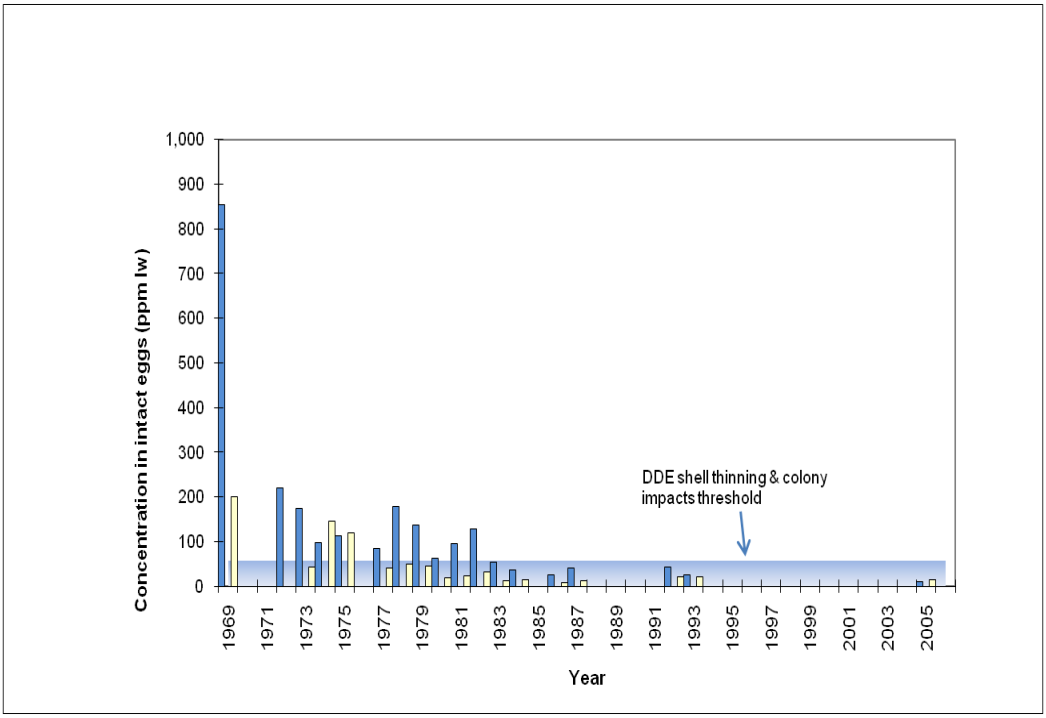
Table 4. Lipid-based concentrations (ng/g lw) of selected organic contaminants detected in brown pelican eggs (geometric mean and range) collected from W. Anacapa Island, California in 1993 and 2005.

Analyte	1993	2005
lipid (% ww)	2.3 (1.6 - 3.0)	2.9 (2.1 - 4.3)
Total DDT	61,533 (18,206 - 460,342)	20,309 (9,012 - 75,753)
DDE	58,024 (17,122 - 451,265)	19,167 (8,346 - 73,638)
PCB-TOTAL	51,256 (15,864 - 131,314)	24,734 (10,135 -58,844)
PBDEs	5,086 (1,119 - 21,539)	4,579 (1,889 - 22,120)
chlordanes	2,497 (799 - 5,960)	1,047 (490 - 2,218)
dieldrin	689 (406 - 1,795)	455 (114 - 868)
sum BHC	492 (314 - 824)	337 (193 - 818)
endrin	156 (101 - 319)	135 (60 - 336)
HCB	9,157 (4,059 - 21,829)	8,961 (3,177 - 16,505)

Gress (1995) evaluated fw-based concentrations of DDE and PCBs in eggs collected from WAI between 1969 and 1992. Mean concentrations measured in eggs collected between 1977 and 1992 by Gress (1995) are compared with results reported by Anderson et al. (1975; 1977), and results from this study in Figure 5. An average lipid fraction of 5.3% observed in studies by Gress (1995) was used to convert fw-based DDE and PCB concentrations reported by Gress (1995) to lw-based values, for direct comparison with concentrations reported by Anderson et al. (1975; 1977) for eggs collected between 1969 and 1977. A detailed analysis of the data collected and compiled by Gress (1995) is in progress and is pending publication elsewhere. Mean concentrations reported in earlier studies (Gress 1985; Anderson et al. 1975; 1977) combined with mean concentrations observed in this study reflect a long-term continuing decline in DDE concentrations (Figure 5). Differences in lw-based concentrations are approximately 2-fold between 1975 and 1993 (Figure 5) and 2.4-fold between 1993 and 2005 (Table 4). Some of the decline observed between 1975 and 1993 may reflect differences between contaminant

levels that occur in failed eggs (1975) and those that occur in viable eggs (1993 and 2005). However, in this regard, the data for 1993 and 2005 are directly comparable, and exhibit a decline that is statistically significant (Table 3; p = 0.0002 for DDE).

Figure 5. Geometric mean DDE (dark bars) and total PCB concentrations (light bars; ug/g or ppm- lipid weight) in intact brown pelican eggs collected from W. Anacapa Island, California, 1969 - 2005*.



* 1969 – 1975, from Anderson et al (1975, 1977), eggs intact but failed to hatch (PCB = aroclors)
1977 – 1987, from Gress (1995), eggs intact but failed to hatch (PCB = Σ7 congeners x 2)
1992 from Gress (1995), eggs intact and viable (PCBs = Σ40 congeners)
1993 & 2005, this study, eggs intact and viable (PCB = Σ>69 congeners, or as homologs, or as aroclor)

The total DDT and p,p'-DDE concentrations measured in viable pelican eggs collected from WAI in 1993 and 2005 are within ranges reported for eggs collected in comparable years from other piscivorous seabird species nesting on the west coast of North America (Zeeman et al. 2008; Harris et al. 2005). Mean concentrations of DDE in eggs of double crested cormorants (*Phacrocorus auritus*) collected in 1993 from the Pacific coast of Canada ranged from 370 to 2,230 ng/g, with the higher concentrations occurring in eggs from nests near industrial areas (Harris et al. 2005). DDE concentrations measured in pelican eggs collected in the same year from WAI range from 455 - 12,726 ng/g fw, and only two of the eggs had concentrations greater than 2,000 ng/g fw. With few exceptions, DDE concentrations measured in the pelican eggs from 1993 were very similar to concentrations observed in double-crested cormorants nesting near industrial areas along the Pacific coast of Canada.

The mean total DDT concentration measured in WAI pelican eggs collected in 2005 (566 ng/g fw) is mid-range for concentrations measured in failed eggs collected the same year from black skimmers (*Rhynchops niger;* mean 1,819 ng/g), Caspian terns (*Sterna caspia*; mean 1,846 ng/g), elegant terns (*Sterna elegans*; mean 555 ng/g) and California least terns (*Sternula (Sterna) antillarum browni*; 402 ng/g fw) nesting in colonies at San Diego Bay (Zeeman et al. 2008). The data from Zeeman et al. (2008) are for failed to hatch eggs, and contaminant levels in viable eggs might have been lower. If such is the case, DDT concentrations in viable pelican eggs from 2005 may be more like DDT concentrations in black skimmers or Caspian terns, rather than in elegant terns. Region-scale comparisons are difficult because contaminant levels measured in seabird eggs can vary widely, depending on the species, the specific nesting location, food source and other factors. However, concentrations of DDT measured in pelican eggs from WAI appear to be roughly typical for seabirds nesting near industrial areas along the Pacific Coast of North America.

Using data on nesting colonies from WAI and on the east coast of the United States, Blus (1984) identified a number of concentration benchmarks for DDE in pelican eggs that are associated with reproductive impairments. Examples of reproductive impairment by DDTs, as well as PCBs and other organochlorine compounds include reduced egg production, defective eggshells, reduced hatchability, embryotoxicity, aberrant incubation behavior by adults, and mortality of chicks and adults (Blus 1996; Hoffman et al. 1996; Gress 1970). In birds, the common, and possibly the most sensitive adverse reproductive effect associated with exposure to DDT, and especially its metabolite DDE, is eggshell thinning. Effect levels identified by Blus (1984) are for colony-level impacts, resulting mostly from crushed eggs, and to a lesser extent from reduced pre- and post hatch survival of young. In his analysis:

(1) 3,000 ng/g fw was the lowest level of DDE in eggs that would result in severely lowered reproductive success and population decline if continued over years;

(2) Total reproductive failure occurred when DDE residues in eggs exceeded 3,700 ng/g fw;

(3) There was a small decrease in nest success when DDE concentrations were between 2,000 ng/g fw and 3,000 ng/g fw (mostly with concentrations between 2,600 ng/g fw and 3,000 ng/g fw); and,

(4) The percent of successful nests associated with concentrations below 2,000 ng/g fw could not be distinguished from percent nest success observed with DDE concentrations below the analytical detection limit.

Blus (1984) also evaluated the relationship between DDE concentration and the critical level of eggshell thinning. The critical level was determined to be $\geq$18% and the corresponding DDE concentration was 5,000 ng/g fw. Pelican eggs with approximately 1,000 ng DDE/g fw may exhibit between 5% and 10% thinning (Blus 1996).

Total DDT concentrations (which were nearly 100% DDE) measured in pelican eggs from 1993 ranged from 484 ng/g fw to 12,982 ng/g fw. Within that range, DDT concentrations in two eggs were >9,800 ng/g fw, concentrations in eight eggs were between 1,000 and 2,000 ng/g fw and concentrations in the remaining five eggs were <1,000 ng/g fw. Using thresholds identified by Blus (1984), at least a subset of the eggs collected in 1993 had DDT concentrations sufficient to result in critical eggshell thinning and reduced success for the individual nests. The mean DDT concentration (approximately 1,400 ng/g fw), and DDT concentrations in 13 out of 15 of the individual eggs collected in 1993 were in the range that impairments, if they occurred, could not be detected based on nest success (fledging rate). The mean total DDT concentration in eggs collected in 2005 was significantly lower than the mean observed in 1993 and none of the 15 eggs from 2005 had total DDT concentrations greater than 2,000 ng/g fw. All but four eggs had concentrations less than 1,000 ng/g.

Based on the analysis by Blus (1984), DDE concentrations measured in at least two eggs from 1993 were expected to result in significant eggshell thinning (>5,000 ng/g fw), and DDE concentrations in eight eggs were near 1,000 ng/g fw and therefore expected to cause 5% to 10% thinning. In 2005, only four eggs had DDE concentrations near 1,000 ng/g fw and therefore expected to result in 5% to 10% thinning. Concentrations in the remaining eggs were well below levels where thinning would be detected (mean 428 ng/g fw). The amount of thinning actually observed in this study corresponded only roughly with DDE concentrations in eggs. The mean percent thinning observed in 1993 (approximately 6%) corresponded with a mean DDE concentration of 1,073 ng/g fw for all but the two most contaminated eggs, and the mean percent thinning observed in eggs from 2005 (0%) corresponded with a mean DDE concentration of 532 ng/g fw. However, no statistically significant correlation could be identified between eggshell thickness and DDE concentration, when evaluated on an egg-by-egg basis. At 9,896 ng/g fw and 12,722 ng/g fw, the two most contaminated eggs had much higher DDE concentrations than the rest of the eggs. Yet, while the most contaminated egg exhibited the greatest thinning (10.5%) the second most contaminated exhibited only average thinning (6%). The percent thinning in the two most contaminated eggs was less than the more than 20% thinning expected from the analysis by Blus (1984), but is within the range of values for individual eggs with approximately 10,000 ng/g fw (range between 10% and 30% thinning). Finally, eggs with the thick shells (>0.600 mm) had DDE concentrations ranging from 350 ng/g fw to 1,628 ng/g fw.

Earlier studies have demonstrated a significant inverse correlation between the DDE concentration and eggshell thickness (Risebrough 1972; Blus et al. 1971; Blus 1984). The analysis by Blus (1984) included data for 813 eggs, with DDE concentrations ranging from approximately 100 ng/g fw to 100,000 ng/g fw (3 orders of magnitude), and most occurring in the 600 to 6,000 ng/g fw range. The sample size in this study is much smaller (N=30), the DDE concentration range is from 300 - 12,722 ng/g fw (1.7 orders of magnitude), with all but two in the 300 - 2,000 ng/g fw range. The lack of a significant correlation in this study may reflect: (1) statistical limitations due to small sample size, (2) statistical limitations imposed by the narrow range of DDE concentrations, (3) that DDE concentrations are becoming too low for a quantitatively demonstrable impact on

shell thickness and / or (4) shifts in the population that may be altering the relationship between DDE concentrations and eggshell thinning.

B. PCBs

Total PCBs were the second-most prevalent of the organic contaminants measured in pelican eggs. Total PCB concentrations measured as aroclors were comparable to concentrations of total PCBs determined as the sum of the homologs and as the sum of the 96 individual congeners (Table 5).

Analytical methods for PCBs have evolved over time; in earlier studies total PCB concentrations were measured against aroclors standards only. Analytical results based on aroclors reflect how well the composition of the aroclor mixtures used for standards captured the composition of the PCB mixtures in the samples, which introduces uncertainty when attempting to compare total PCB concentrations in one study with total PCB concentrations in other studies. Recognizing that the composition of aroclor standards themselves can vary, the percent contributions of PCB homolog classes to total PCB concentrations in pelican eggs from this study are roughly comparable to approximate homolog compositions for aroclors 1260 and 1262 (Table 6), which are dominated by penta-, hexa and heptachlorobiphenyls, with small contributions from octa- and nona-chlorobiphenyls. In this study, the total PCB results based on aroclor standards offer a reasonable estimate of the total PCB concentration, and may be compared to results of earlier studies that used aroclors 1260 and 1262 as standards for quantifying exposure and for assessing toxic levels of PCB mixtures.

Table 5. Concentrations of total PCBs measured as the sum of aroclors, congeners, and homologs in brown pelican eggs collected from W. Anacapa Island, California, in 1993 and 2005.

ppb fresh weight	1993			2005		
	geomean	min	max	geomean	min	max
Total PCBs as Aroclors	1,170	377	3,161	716	395	1,538
Total homologs	1,173	379	3,161	719	399	1,537
Total PCB Congeners	1,235	401	3,392	757	418	1,568
No. congeners detected (out of 93)		75	84		69	83
Σ 7 congeners*	442	129	1,395	264	93	686

* Congeners #101, 118, 138, 153, 170, 180, 195. For comparison with results from Gress (1995, details pending publication elsewhere)

In more recent studies by Gress (1995), total PCB concentrations in pelican eggs were evaluated as either [(Σ concentrations for 7 individual congeners) x 2], or as (Σ concentrations for 40 individual congeners), depending on the year the eggs were analyzed (Figure 5). Total PCB concentrations obtained by Gress (1995) when eggs were analyzed for 40 congeners, were approximately double the results obtained when eggs were analyzed for only 7 congeners, and therefore supported the use of the factor of two when relying on data for 7 congeners only. A detailed analysis of the results obtained by Gress (1995) is pending publication elsewhere. However, at this time it can be noted that

total PCB concentrations observed in this study as aroclors, homologs and Σ>69 congeners, are approximately 2.7 times greater than the sum of the concentrations of the 7 congeners used in earlier studies (Table 5).

Most of the 93 target PCB congeners were detected in one or more samples (N>75 in 1993 and N>69 in 2005; Table 3). The maximum percent contribution for any single congener to the total PCB concentration was approximately 10%, and contributions from most that were detected were less than 2%. Approximately 80% of the total for each sample was contributed by 27 congeners with 5, 6 or 7 chlorine atoms. With only a few exceptions, all of the congeners in this range were detected in more than 12 and typically all 15 of the samples from both years. The most prevalent congeners (those contributing more than 5%) were in decreasing order PCB #153 (co-eluted with PCB #132), PCB #180, PCB #138 (co-eluted with PCB #160), PCB #92 and PCB #82. Congeners 153, 138 and 180 are also the most commonly detected congeners detected in fish tissue samples (ATSDR 2000), and in eggs of other seabird species (Braune 2007).

Table 6. Mean homolog concentrations (ng/g or ppb fw), detection frequencies and percent contributions of each class to the total PCB concentrations in brown pelican eggs collected from W. Anacapa Island, California in 1993 and 2005, as compared the homolog distributions in aroclor mixtures.

	1993			2005			Approximate percent contributions of homolog classes to Aroclor mixtures*				
Homolog Class	mean concentratin (ppb fw)	detects (N=15)	**percent contribution**	mean concentration (ppb fw)	detects (N=15)	**percent contribution**	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Aroclor 1268
Cl1-PCB			**<1**		1	**<1**					
Cl2-PCB		1	**<1**	4.33	5	**0.5**					
Cl3-PCB	6.53	9	**<1**	8.87	13	**1.3**	~21				
Cl4-PCB	73.4	15	**5.1**	45.1	15	**5.8**	~33	~7	~9		
Cl5-PCB	408	15	**29**	216	15	**28**	~43	~65	~43	~3.4	
Cl6-PCB	524	15	**36**	288	15	**34**		~24	~39	~26	
Cl7-PCB	321	15	**22**	206	15	**24**			~8	~48	~12
Cl8-PCB	76.2	15	**5.1**	45.3	15	**5.5**				~20	~45
Cl9-PCB	12.8	15	**1.2**	8.79	14	**1.1**				~2	~38
Cl10-PCB	3.44	10	**0.24**	3.21	6	**0.4**					~5
Total	1,430			829							

*From ATSDR 2000 and Maruya et al. 1997 (Aroclor 1268)

PCB congeners with chlorines in the non- or mono-ortho position have dioxin-like toxicity. All but one (PCB #114) of the dioxin-like congeners (non-ortho PCB #77, #81, #126 and #169, and mono-ortho PCB#105, #114, #118, #156, #157, #167, and #189) were detected in one or more samples, albeit at low concentrations. While none of the dioxin-like congeners were major contributors to the total PCB concentration, they were the sole contributors to TEQ concentrations in all but a few samples because dioxins and furans were consistently below the limited of detection (Table 7).

Table 7. TEQ concentrations (pg/g fw) of dioxin-like PCB congeners and detected PCDDs/PCDFs in brown pelican eggs collected from W. Anacapa Island, California in 1993 and 2005.

	1993		2005	
	geometric mean (range)	detects (N=15)	geometric mean (range)	detects (N=15)
PCBs				
PCB# 77	35.3 (6.10 - 79.0)	15	32.2 (12.2 - 70.0)	15
PCB# 81	80.5 (34.9 - 361)	15	48.8 (20.4 - 117)	15
PCB# 126	22.5 (1.4 - 124)	14	16.8 (9.30 - 34.1)	15
PCB# 169	0.166 (0.058 - 0.467)	15	0.258 (0.139 - 0.471)	15
PCB# 105	1.38 (0.407 - 4.66)	15	0.690 (0.312 - 1.99)	15
PCB# 114	<0.002	0	<0.002	0
PCB# 118*	0.507 (0.165 - 1.51)	15	0.287 (0.130 - 0.751)	15
PCB# 156	0.666 (0.178 - 2.86)	15	0.041 (0.002 - 0.848)	9
PCB# 157/173/201	0.470 (0.108 - 1.63)	15	0.316 (0.067 - 0.796)	15
PCB# 167	0.070 (0.014 - 0.263)	15	0.035 (0.012 - 0.145)	15
PCB# 189	0.005 (0.0002 - 0.040)	15	0.001 (0.0002 - 0.018)	7
PCDDs/PCDFs[1]				
1,2,3,4,6,7,8-HpCDD	- (<0.020 - 0.062)	1	<0.024	0
OCDD	- (<0.004 - 0.029)	2	- (<0.005 - 0.025)	1
2,3,7,8-TCDF	- (<4.00 - 12.0)	1	<5.00	0
OCDF	- (<0.004 - 0.026)	2	<0.005	0
TEQ_{PCB}	150 (58.0 - 510)		101 (48.0 - 201)	
TEQ_{TOTAL}	152 (58.0 - 510)		101 (48.0 - 203)	

1. Not detected in any samples = 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF.
2. PCB 118 may be an overestimate, and its contribution to total TEQ concentration may be less than indicated.

Out of 30 eggs, four had measurable levels of selected PCDDs/PCDFs; one with detectable levels of HpCDD, OCDD, OCDF and TCDF; two with detectable levels of OCDD, and one with detectable level of TCDF. Even when PCDDs/PCDFs were

detected, PCB congeners were the primary contributors to the TEQ concentration with percent contributions ranging from 85% in one egg to 98% in three and 100% in the remaining 27 eggs.

Among the PCBs, congeners #77, #81 and #126 contributed more than 90% to the total TEQ. Of those, congener #81 consistently contributed the most, followed by congener #77 and then congener #126. Simple concentrations of those congeners exhibited the same relative abundances. The observed pattern of relative contributions is unusual for avian eggs, because avian species can metabolize and eliminate PCB #77, and therefore do not typically accumulate that congener in their tissues. PCB# 77 was reported as the dominant dioxin-like congener in one study on raptors (Weismuller 2002), and was interpreted as a potentially limited capacity in some wild bird species to convert PCB #77 to hydroxyl compounds. PCB #77 tends to occur at higher concentrations than PCB #126 in freshwater fish (Satyendra et al. 2007), but similar data are lacking on congener profiles in marine fish. The relative contributions of PCBs #77, #81, and #126 in the pelican eggs may reflect what is in the fish that they eat, combined with decreased capacity for metabolizing PCBs #77. Alternatively, concentrations of these congeners in most eggs ranged from less than 10-times to approximately 30-times detections limits, and as such may be considered low. The unusual relative contributions may reflect analytical artifacts and uncertainty that occur when concentrations are near detection limits.

Total PCB concentrations in eggs of pelicans from WAI declined significantly between 1993 and 2005 (Table 3). Compared with the lw-based values summarized by Anderson et al. (1977; 1975) and Gress (1995), PCB concentrations measured in eggs from 1993 and 2005 reflect an ongoing long-term gradual decline since the mid-1970s (Figure 5). The earliest data on PCB levels in pelican eggs are for Aroclor 1260, and as such are comparable to results from this study. According to Anderson et al. (1977), the mean lipid-based PCB concentration in pelican eggs collected from WAI in 1975 was 146,000 ng/g lw, which is nearly 3-times the concentration in 1993, and nearly 6-times the concentration in 2005. Gress (1995) obtained data on PCB concentrations for intervening years (1977 - 1992), and a detailed analysis of those results is in progress, pending publication elsewhere.

Like DDT, the mean total PCB concentration measured in viable WAI pelican eggs from 2005 (710 ng/g fw) is comparable to concentrations reported for failed eggs of elegant terns (651 ng/g) and California least terns (949 ng/g) nesting the same year in south San Diego Bay (Zeeman et al. 2008). Mean concentrations of total PCBs in eggs of double crested cormorants collected in 1993 from the Pacific coast of Canada ranged from 800 to 2,340 ng/g, depending on the nest location (Harris et al. 2005). The range of concentrations measured in the pelican eggs from WAI in 1993 (377 - 3,161 ng/g fw) overlaps with the range (800 - 2,340 ng/g fw) observed with double-crested cormorants nesting at a variety of locations, including some near industrial centers, along the Pacific coast of Canada. Region-scale comparisons are difficult because contaminant levels measured in seabird eggs can vary widely, depending on the species, the specific nesting location, food source and other factors. However, concentrations of PCBs measured in

pelican eggs from WAI appear to be typical for seabirds nesting near industrial areas along the Pacific coast of North America.

Unlike other seabirds, total PCB concentrations measured in pelican eggs from WAI have historically been secondary to DDT/DDE concentrations. The ratio of total DDT to total PCBs reflect the relative importance of the two dominant contaminant classes measured in pelican eggs. The DDT/PCB ratios shifted from a mean of 1.20 in eggs from 1993 to a mean of 0.80 in eggs from 2005. The ratios are approximately 4 times lower than DDE/PCB ratios observed in WAI pelican eggs from 1969 and 1970 (ratio = 4.0; Anderson et al. 1977) and are comparable to DDE/PCB ratios reported for eggs collected from WAI in 1974 and 1975 (Anderson et al, 1977; ratios 0.7 and 0.9, respectively). Even though the DDT/PCB ratios in pelicans from WAI have declined over time, they are still higher than DDE/PCB ratios observed in eggs of double crested cormorants collected between 1970 and 1998 (ratios approximately 0.10 - 0.30) from the Pacific coast of Canada (Elliott et al. 1989; Harris et al. 2005). While the PCB levels measured in WAI pelican eggs collected in 1993 and 2005 appear to be typical for seabirds nesting near industrial areas, the DDT/PCB ratios observed in eggs collected for this study reflect significant ongoing influences of local DDT sources along the coast of southern California. However, although not statistically significant, the shift suggests that PCBs are becoming the predominant OC contaminant for pelicans that nest and forage in the SCB which has been heavily dominated by DDTs since the 1960s.

The PCB concentrations measured in pelican eggs were below approximately 3,200 ng/g (max; mean = 1,170 ng/g) in 1993 and below approximately 1,600 ng/g (max; mean = 716 ng/g) in 2005. Embryo toxicity is a common sensitive adverse effect associated with in ovo exposure to PCBs. Total PCB concentrations greater than 5,000 ppb have been associated with reduced hatching in chickens, which are among the most sensitive of the avian species (Hoffman et al. 1996). Total PCB concentrations between 6,000 ppb and 26,000 ppb have been associated with reduced hatchability in wild populations of Forster's tern (Hoffman et al. 1996). Custer et al. (1999) observed no effects on embryo survival or incidence of abnormalities in field populations of cormorants with 12,000 ng/g total PCBs in the eggs. The total PCB concentrations measured in pelican eggs from WAI were below effect levels reported for embryo toxicity and reduced hatching success in sensitive avian species (chickens) and well below potential effect levels for seabirds in the same order (Pelicaniformes) and with similar feeding habits as pelicans (i.e., cormorants).

The maximum TEQ concentrations in pelican eggs from WAI (510 ng/g in 1993 and 210 pg/g in 2005) may exceed effect levels in the most sensitive avian species (chickens) but are well below levels associated with adverse effects in cormorants. Powell et al. (1997) observed no effect on double-crested cormorant embryos when eggs were injected with extract containing 325 pg TEQ / g. Using injection with PCB 126, Powell et al. (1997) ascertained that cormorant embryos are considerably less sensitive than chickens to dioxin-like PCBs, and estimated that the median lethal TEQ concentration for cormorant embryos is between 5,000 and 26,000 pg/g. Based on 2,3,7,8-TCDD toxicity, the lowest effect TEQ level in cormorants is approximately 4,000 pg/g.

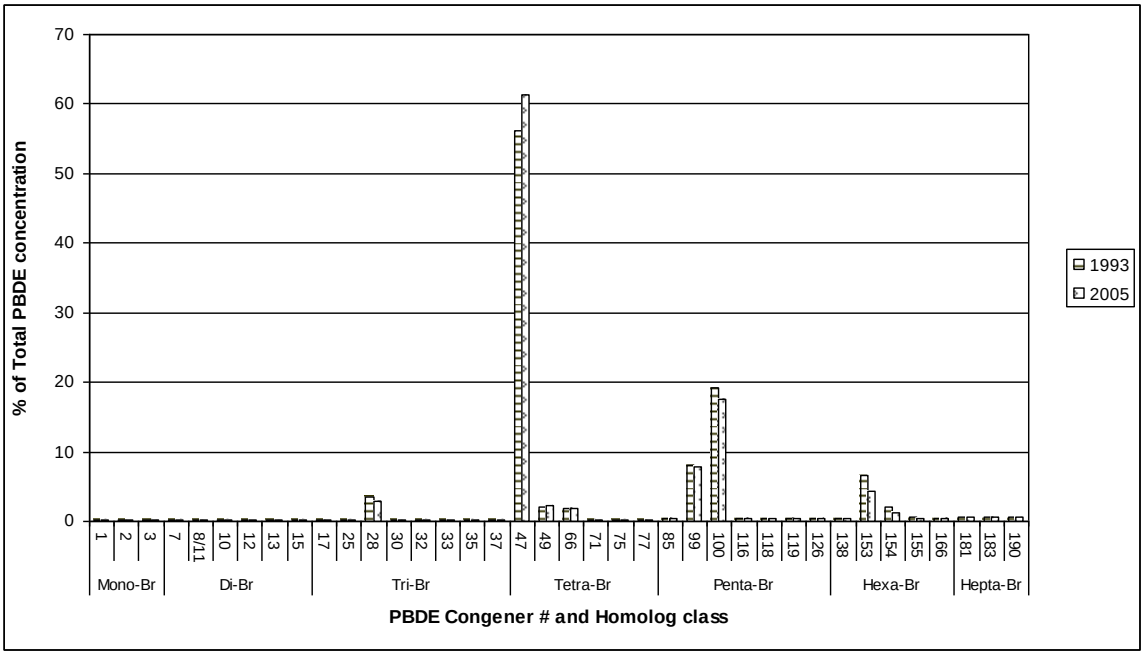
C. PBDEs

After DDT and PCBs, PBDEs were the third greatest contributor to the total organic contaminant load in pelican eggs from WAI (Table 3), and individual congeners were detected in all 30 egg samples. However, of the 38 congeners that were targeted, only 12 were detected in one or more samples (Figure 4). Of those, the predominant congeners were BDE #47 (average = 58% of the total), followed by BDE #100 (average = 19% of the total), BDE #99 (average = 8% of the total) and BDEs #153, #49, #28, #66 and #154. BDEs #17, #118, #119 and #155 were also detected, but very infrequently and at low concentrations.

In addition to being the predominant congeners in the pelican eggs, BDE congeners #47, #99, and #100 are also the predominant congeners in the commercial mixture, penta-BDE that was produced and used in many household and commercial products until 2004, when uses of the penta-BDE and the octa-BDE mixtures in the U.S. were banned (ATSDR 2004). The pelican eggs were not analyzed for deca-BDE (100% BDE-209), which is still in use. BDE-209 has been detected in eggs of seabirds nesting at San Francisco Bay, but at very low concentrations (She et al. 2008). Potential reasons for the low concentration of deca-BDE include (1) it is not present in the system, (2) it is present but substantially debrominated once in the environment, or (3) bioaccumulation of deca-BDE may be low for seabirds due to exposure pathways and / or metabolism specific to seabird species. Because deca-BDE is still in use, and because it can be found in seabird eggs, albeit at low concentrations, this congener should be included among the target analytes in future studies that monitor PBDE exposure by seabirds.

Total PBDE concentrations measured in pelican eggs from WAI did not change between 1993 and 2005 (Table 3). The time elapsed between when the use of penta-BDE in the U.S. was banned (2004) and when the eggs were collected (2005) may have been too short for changes in PBDE accumulation by pelicans to be evident. While new uses of penta-BDE are banned, the many commercial products to which the mixture was added are still in use and releases of PBDEs to the environment may increase as the PBDE-bearing products enter the waste stream. Therefore, even with the ban on new use, it is not certain that PBDE concentrations in pelican eggs will fall in the immediate future.

Figure 6. Relative contributions of individual PBDE congeners to total PBDE concentrations in brown pelican eggs collected from W. Anacapa Island, California in 1993 and 2005.



Due to QA/QC anomalies, concentrations and therefore relative contributions of BDE #s 28, 66, 85, 99, 100, 153, and 154 may be overestimates.

Total PBDE concentrations measured in pelican eggs collected from WAI do not stand out as unusually high or low for seabirds that nest off the coast of California. The lipid-normalized PBDE concentrations measured in eggs from 2005 (1,889 ng/g lipid - 22,120 ng/g lipid; mean = 4,579 ng/g lipid) are within ranges reported for Caspian terns and California least terns from San Fransisco Bay (She et al. 2008), and for elegant terns and Caspian terns from San Diego Bay (Zeeman et al. 2008). The PBDE concentrations observed in pelican eggs from WAI appear to be lower than concentrations measured in eggs of black skimmers (mean = 17,360 ng/g lipid) and higher than in eggs of California least terns (mean = 2,210 ng/g lipid) collected from colonies at San Diego Bay in 2005 (Zeeman et al. 2008). The PBDE concentrations reported by Zeeman et al. (2008) are for non-viable eggs, and as such may overestimate concentrations in viable eggs. However, the differences are not expected to be sufficient to alter the roughly comparable nature of PBDE concentrations in viable pelican eggs and those in eggs of other seabird species.

PBDEs alter blood thyroid hormone homeostasis and / or vitamin A stores, which in turn can alter development, immuno-competence, reproductive success and other physiological process. Studies by Fernie et al. (2005) indicate that the endocrine disruption can occur in kestrels exposed to environmentally meaningful concentrations of PBDEs (approximately 1,500 ng/g wet weight in the egg, and the equivalent of 100 ng/g wet weight in the post-hatch diet). In a subsequent study, Fernie et al. (2009) determined

that eggs with PBDE concentrations of 300 ppb and 1,130 ppb fw were significantly smaller and weighed less than eggs in a control group (3 ppb PBDE). Shells of eggs with the higher PBDE concentration were significantly thinner than controls and the weights of eggs with 300 ppb PBDE were significantly lighter than controls. The PBDE concentrations measured in pelican eggs for this study are much lower than apparent effect levels associated with impacts on endocrine function in kestrels. The mean PBDE concentrations measured in the pelican eggs were less than 300 ng/g fw and out of the thirty tested, only four individuals had concentrations greater than 300 ng /g fw (max = 607 ng/g fw; Table 3). As such, the PBDE levels measured in pelican eggs are between a no effect level and a low effect level for reduced egg size and for shell thinning in kestrels. Shells of pelican eggs collected in 1993 exhibited some thinning (Table 2). However, no correlation was found in this study between PBDE concentration and shell thickness, shell weight or the size of pelican eggs (Table 1). The lack of correlation may be due to statistical limitations (narrow range of concentrations). Alternatively, the PBDE concentrations observed in this study are below low effect levels for sensitive avian species (kestrels) and may be too low to have measurable effects on egg size and shell thickness in pelicans.

D. Other organochlorine compounds

Organochlorine compounds other than DDT and PCBs occurred at relatively low concentrations. Concentrations of most of the non-DDT and PCB OC compounds ranged from <10 ng/g fw to <100 ng/g fw (Table 3). Concentrations of BHCs, mirex, dieldrin and chlordanes measured in pelican eggs collected in 1993 and in 2005 fall within ranges observed in eggs of double-crested cormorants collected off Pacific coast of Canada in 1993 and 2002 (Harris et al. 2005). Concentrations of the non-DDT and PCB OC compounds measured in pelican eggs from 2005 are also roughly comparable to concentrations of the same analytes measured in failed eggs of Caspian terns and black skimmers collected from San Diego Bay colonies in 2005 (Zeeman et al. 2008). One exception was tetrachlorobenzenes, which occurred at much higher concentrations in San Diego Bay seabirds (12 ng/g - 26 ng/g) than in eggs of pelicans from WAI (<2 ng/g fw; this study). Concentrations are low, but differences such as those evident with tetrachlorobenzene may be considered as evidence of local influences and /or species differences in diet or physiological process that affect accumulation.

For many OC compounds, data on concentrations in eggs associated with adverse effects are limited at best. It is recognized that thresholds may vary according to species and data on effect levels for an individual species (e.g., pelicans), and data on effect levels even for other species may be very limited to nonexistent, depending on the contaminant.

While there have been a few studies on levels in the diet that are toxic, data relating chlordane concentrations, and its metabolite oxychlordane, in eggs to reproductive effects are lacking (Wiemeyer 1996). Data relating concentrations of tetrachlorobenzenes and pentachloroanisole in eggs to reproductive effects are also lacking. Even though concentrations of these OC compounds are low, conclusions about their potential for having adverse effects are not possible at this time. It is noted, however that

concentrations of tetrachlorobenzenes and pentachloroanisoles increased significantly between 1993 and 2005. Tetrachlorobenzenes are no longer produced commercially but may still enter the environment as waste from past uses as a dielectric fluid in transformers, as a precursor in the production of herbicides and other organic compounds and as moisture-proofing for electrical insulation (USEPA 1992). Pentachloroanisole has no commercial applications, but its presence as an environmental contaminant is widespread, probably because it is a metabolic product of pentachlorophenol which was commonly used for wood preservation (USEPA 1992).

Blus (1982) evaluated relationships between OC compound concentrations in eggs of pelicans from the east coast of the United States and reproductive effects, using measures of nest success. It was not possible to clearly discern critical levels for OCs other than DDE. Without establishing a specific critical level, Blus (1982) did determine that the effect level for dieldrin in pelican eggs would be >1,000 ng /g fw and the effect level for endrin was roughly estimated to be <500 ng/g fw. Effect levels for dieldrin in eggs of double-crested cormorant also appear to be >1,000 ng/g (Custer et al. 1999). In a study by Roylance et al. (1985), the endrin concentration associated with reduced embryo survival in mallards was 2,750 ng/g and no effect was observed at the next lowest concentration of 430 ng/g. These are orders of magnitude greater than the concentrations of dieldrin and endrin that were measured in pelican eggs collected for this study.

Because heptachlor is readily metabolized to heptachlor epoxide in vertebrates (Wiemeyer 1996), most of the data on toxicity of heptachlor is for heptachlor epoxide. Blus et al. (1984) observed that nest success for Canada goose exposed to heptachlor epoxide was unaffected when eggs contained up to 10,000 ng/g ww. Heptachlor epoxide concentrations associated with adverse effects appear to be >1,500 ng/g in kestrels, >10,000 ng/g in Japanese quail and about 3,000 ng/g to 7,000 ng/g in grey partridge (Wiemeyer 1996). Concentrations of heptachlor and heptachlor epoxide measured in pelican eggs for this study (all <10 ng/g fw) are well below levels associated with adverse reproductive effects in other avian species.

Little if anything is known about the toxicity of BHC, particularly β-BHC, which is the isomer that is retained and accumulated in animal tissues. In general, BHC is considered not very toxic to avian embryos (Wiemeyer 1996). The limited data are on γ-BHC (lindane), which is the most active as an insecticide of the isomers. In two studies, no effects were observed even when concentrations of γ-BHC in eggs were as high as 10,000 ng/g for ring-necked pheasant (Blus et al. 1984) and 5,500 ng/g for American kestrel (review by Wiemeyer 1996). There are no data to indicate if pelicans, or seabirds in general are more sensitive than upland species or raptors. However, the BHC concentrations measured in pelican eggs are orders of magnitude lower than no effect levels for BHC in other species, and therefore are of minor concern at this time.

Hexachlorobenzene is one of the analytes that occurred at a higher concentration in 2005 than in 1993. However, concentrations appear to be well below levels identified as NOAELs for survivability of herring gull chicks in an egg injection study by Boersma et al. (1986) (1,500 ng/g ww) and in a wild population of Canada goose whose reproduction

was unaffected even when HCB concentrations in eggs were as high as 2,970 ng/g ww (Blus et al 1984).

3.3 Inorganics

Silver, beryllium, cobalt, molybdenum, and vanadium were below the limits of detection in all samples and boron, chromium and nickel were detected rarely. Boron and chromium were detected very infrequently, and when they were detected it was at concentrations close to the limits of detection. Cadmium, silicon and titanium were detected rarely in eggs collected one year and frequently in eggs collected the other year. The remaining inorganics were detected frequently, if not in all samples from both years (Table 8).

Of the detected inorganic analytes, calcium, magnesium and phosphorus were significantly higher ($p = 0.05$) in 2005 than in 1993. Higher calcium, magnesium and phosphorus concentrations occurred in eggs collected in both 1993 and 2005 with late stage embryos. All of the eggs collected in 2005 had late-stage embryos, for higher average concentrations, whereas eggs collected in 1993 had a mix of developmental stages (Table 1 and Figure 7), for lower average concentrations. Calcium concentrations are plotted as a function of developmental stage in Figure 7. Concentrations of both phosphorus and magnesium were significantly correlated with the calcium concentrations ($r = 0.733$ for phosphorus and $r = 0.625$ for magnesium, df for each = 28). All three of these minerals are primary components of bone. Consequently, the differences between concentrations of Ca, P and Mg observed in 1993 and 2005 probably reflect increased demand and mobilization of these minerals from the eggshell during the later stages of development.

Mercury, selenium and strontium were detected in all of the eggs at concentrations that declined significantly between 1993 and 2005 (Table 8). All of the mercury in the pelican eggs was as methylmercury, which is typically the dominant form that is accumulated in the tissues of fish and their predators (Eisler 1987). The decline in the mean mercury concentration between 1993 and 2005 is approximately 2.8-fold and may reflect: (1) declines in residual contamination from past releases (e.g., in contaminated sediment); and / or, (2) declines in ongoing releases of mercury with wastes and industrial emissions that are now more stringently regulated. Although statistically significant, changes in mean selenium and strontium concentrations are less than 2-fold and as such are more subtle than the changes observed with mercury. Further monitoring is required to determine if the declines in any of these elements represent a long-term trend.

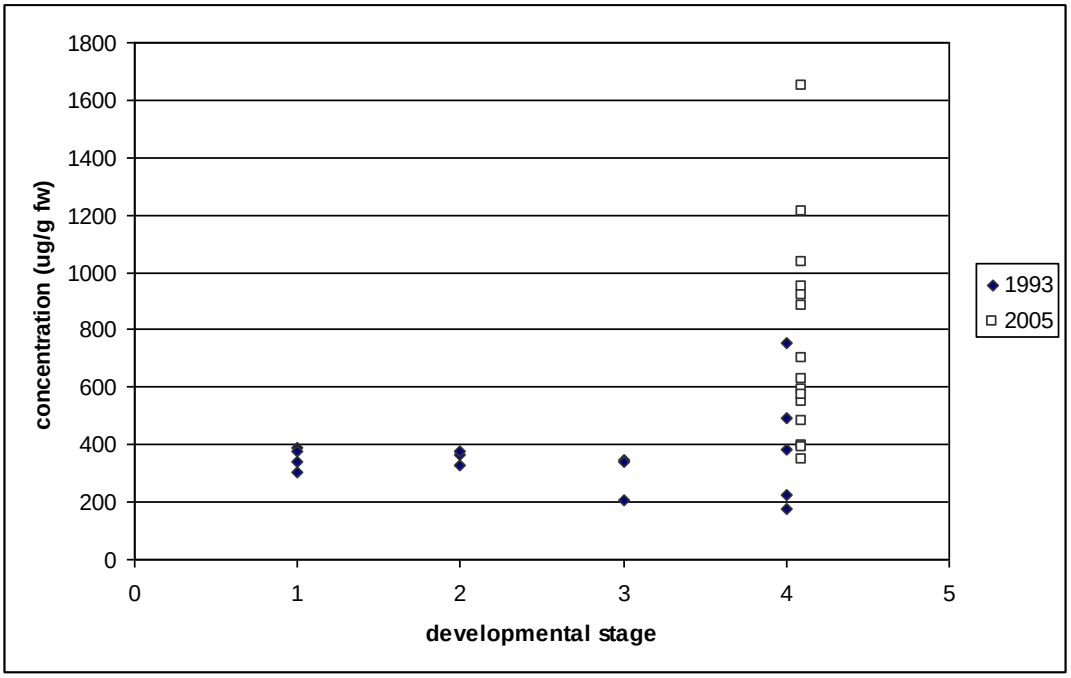
Most of the earlier studies reporting concentrations of metals in avian eggs are focused on elements with documented avian toxicity, most notably mercury, selenium, cadmium and lead (e.g., Ohlendorf 1993).

Table 8. Concentrations (µg/g or ppm fw) of inorganic analytes measured in brown pelican eggs collected from W. Anacapa Island, California in 1993 and 2005.

	1993			2005					
Analyte	Arithmetic mean (and range)		detects (N=15)	Arithmetic mean (and range)		detects (N=15)	mean dl	change (1993 →2005)	significance (Mann-Whitney)
% Moisture	83.1	(81.9 - 84.1)		83.9	(80.0 - 85.3)				
Ag	<0.074		0	<0.074		0	0.074	nt	
Al	0.144	(<0.074 - 0.491)	13	0.186	(0.101 - 0.439)	15	0.074	→	ns
As	0.078	(.056 - 0.098)	15	0.141	(0.096 - 0.199)	15	0.007	→	ns
B	0.094*	(0.074 - 0.118)	6	0.082*	(<0.074 - 0.084)	2	0.074	nt	
Ba	0.046	(<0.015 - 0.086)	13	0.041	(0.024 - 0.074)	15	0.015	→	ns
Be		(0.007 - <0.007)	0	<0.007		0	0.007	nt	
Ca	374	(09 - 752)	15	752	(347 - 1,65)	15	1.023	↑	0.001
Cd	0.002*	(<0.001 - 0.003)	4	0.003	(0.002 - 0.013)	15	0.001	nt	
Co		(0.074 - <0.074)	0		(0.032 - 0.042)	0	0.074	nt	
Cr		(<0.074 - 0.075)	1	0.113*	(<0.074 - 0.239)	5	0.074	nt	
Cu	1.79	(1.00 - 3.62)	15	2.59	(1.11 - 8.82)	15	0.074	→	ns
Fe	18.3	(13.9 - 23.2)	15	20.0	(15.4 - 24.3)	15	0.149	→	ns
Hg (total)	0.328	(0.118 - 0.620)	15	0.117	(0.092 - 0.154)	15	0.000	↓	0.001
Hg (methyl)	0.335	(0.111 - 0.592)	15	0.123	(0.091 - 0.172)	15	0.004	↓	0.001
K	1,268	(1,103 - 1,663)	15	1,214	(990 - 1,459)	15	1.023	→	ns
Mg	95.9	(85.2 - 115)	15	105	(94.8 - 122)	15	0.149	↑	0.002
Mn	0.123	(0.061 - 0.196)	15	0.150	(0.063 - 0.216)	15	0.030	→	ns
Mo	<0.149		0		(<0.149- 0.084)	1	0.149	nt	
Na	1,875	(1,653 - 2,234)	15	1,867	(1,713-2,168)	15	1.023	→	ns
Ni		(<0.074 - 0.103)	1	0.089*	(<0.074 - 0.170)	8	0.074	nt	
P	996	(792 - 1,170)	15	1,115	(880 - 1,588)	15	0.745	↑	0.05
Pb	0.030	(<0.007 - 0.109)	9	0.089	(<0.007 - 0.463)	14	0.007	→	ns
S	1,204	(1,099 - 1,307)	15	1,205	(1,127 - 1,375)	15	0.745	→	ns
Se	0.348	(0.312 - 0.412)	15	0.306	(0.252 - 0.385)	15	0.007	↓	0.005
Si	1.25	(0.750 - 1.61)	12	<1.02		0	1.023	nt	
Sr	0.709	(0.359 - 1.20)	15	0.491	(0.359 - 0.689)	15	0.007	↓	0.05
Ti	0.204*	(<0.074 - 0.371)	5	0.336	(0.126 - 0.673)	15	0.074	nt	
V	<0.074		0	<0.074		0	0.074	nt	
Zn	7.49	(5.81 - 9.46)	15	8.53	(6.29 - 12.0)	15	0.030	→	ns

ns = not significant at $p \leq 0.05$
nt = not tested due to small sample size in one or both years
* = using detects only
to allow for comparison with other studies, ug/g dry weight = ug/g fw x 5.88

Figure 7. Calcium concentrations as a function of developmental stage, in brown pelican eggs collected from W. Anacapa Island, California in 1993 and 2005.



Development stages: 1= fresh or unfertilized, 2 = early, 3 = mid, and 4 = late

Mercury is readily transferred from parent to egg and may reach levels that have adverse effects on developing embryos (Eisler 1987). Concentrations measured in pelican eggs collected for this study are below levels associated with proximity to human use of mercury (1 ug/g fw; Eisler 1987). The mercury concentrations measured in pelican eggs from 2005 are lower than concentrations reported by Zeeman et al. (2008) for failed eggs of black skimmer (0.19 ug/g fw), Caspian tern (0.51 ug/g fw), elegant tern (0.39 ug/g fw) and California least tern (0.24 ug/g fw) collected the same year from colonies in San Diego Bay. Mercury concentrations measured in eggs from 2005 are also below levels considered to be background (<0.2 ug/g fw) for avian eggs in general (USDOI 1998).

Mercury is one of two elements that are most often implicated in cases of impaired avian reproduction. Mercury is a neurotoxin that at high levels of exposure can cause altered behavior, ataxia, appetite loss, weight loss and death. At lower exposure levels it can cause reproductive impairments measured as reduced egg production, egg viability, egg hatchability, embryo survival and chick survival. Mercury concentrations between 0.50 ppm and 2.0 ppm ww in eggs are sufficient to produce the reproductive effects in non-marine birds. However, higher concentrations are required to cause adverse effects in piscivorous seabirds (Thompson 1996; Ohlendorf 1993). Mercury concentrations measured in eggs of pelicans from WAI are below concentrations associated with adverse reproductive effects in sensitive avian species. As seabirds, pelicans are among the less sensitive species and are not expected to exhibit adverse effects from mercury at the observed concentrations.

Selenium is another element that is readily transferred from parent to egg and may reach levels that have adverse effects on developing embryos (Eisler 1985). Concentrations measured in pelican eggs collected for this study (up to 0.40 ug/g fw) are all below concentrations reported by Zeeman et al. (2008) for failed eggs of black skimmer, Caspian tern, elegant tern, and California least tern (means = 0.50 ug/g fw - 0.63 ug/g fw) collected in 2005 from colonies in San Diego Bay. The maximum selenium concentration measured in pelican eggs (0.4 ug/g fw or 2.35 ug/g dw) is within the range considered to be typical of background for avian species (1 ug/g - 3 ug/g dw; Ohlendorf 1993; USDOI 1998).

Selenium is an essential nutrient at low concentrations and is toxic when present at excessive levels. Selenium toxicity in wild birds has been associated with mortality, impaired reproduction (egg hatchability), teratogenesis, and histopathological lesions with alterations in hepatic glutathione (Hoffman 2002). The selenium concentrations observed in eggs from this study are below concentrations associated with adverse effects in sensitive avian species (i.e. 3 - 6 ug/g dw; USDOI 1998).

Cadmium was detected infrequently in pelican eggs, and when it was detected, concentrations were not much greater than the detection limits (Table 8). The highest measured cadmium concentration (0.013 ug/g fw or 0.076 ug/g dw) is comparable to the mean concentration reported for pelican eggs from WAI in 1971 (Risebrough 1972; 0.10 ug/g dw, n=5) and within the range that represents background (<0.5 ug/g dw; Ohlendorf 1993). At less than- to just above detection limits, the cadmium concentrations measured in pelican eggs are comparable to those reported by Zeeman et al. (2008) for failed eggs of black skimmer, Caspian tern, elegant tern and California least tern (all non-detects, except one @ 0.03 ug/g fw) collected in 2005 from colonies in San Diego Bay. The concentrations of cadmium in pelican eggs, and avian eggs in general are expected to be low because, while there may be some transfer to eggs, cadmium taken up by an adult bird is much more likely to accumulate in tissues such as the kidney and liver, than to be deposited in an egg (Furness 1996).

The toxic effects most commonly associated with cadmium exposure include impaired growth, anemia and testicular damage (Eisler 1985). The toxic effects of cadmium in avian species have also included altered avoidance response, reduced egg production, eggshell thinning, kidney damage, damage to the gut epithelium, altered energy metabolism, impaired bone marrow function, heart abnormalities and adrenal abnormalities (Furness 1996; Eisler 1985). These effects, which were observed in laboratory tests, have been related to cadmium levels in the diet, the liver or the kidney. Benchmarks relating adverse effects to cadmium concentrations in eggs are lacking (Ohlendorf 1993), and the likelihood of cadmium reaching levels in eggs is considered to be very low (Furness 1996). Absent the necessary benchmarks, Burger (2002) compared cadmium levels in gull and seabird eggs to concentrations reported for piscivorous birds in general, where adverse effects have not been observed. The median concentration for cadmium in eggs of piscivorous birds exhibiting no effects is 0.015 ug/g ww (Burger 2002), and cadmium concentrations observed in eggs collected for this study (max = 0.013 ug/g ww) are lower. Consequently, the cadmium concentrations observed in

pelican eggs from WAI are considered low, typical of background and appear to be below levels that would result in adverse effects.

Lead was detected in more than 50% of the samples. Lead concentrations in eggs less than 0.50 ug/g dw are considered background (Ohlendorf 1993). Mean lead concentrations measured in pelican eggs from WAI were below or at the limit for background (0.18 ug / g dw in 1993 and 0.52 ug/g dw in 2005; Table 8). Mean values and concentrations in 16 of the 30 individual eggs were greater than 0.10 ug/g dw, which was the upper limit reported for five pelican eggs from the same colony in 1971 (Risebrough 1972). Lead concentrations measured in pelican eggs collected in 2005 are higher than lead concentrations measured in failed eggs collected in 2005 from San Diego Bay colonies of black skimmer, Caspian terns, elegant tern, and California least terns (< 0.06 ug/g ww for all species; Zeeman et al. 2008). Dry weight-based concentrations of lead measured in pelican eggs from 1993 (maximum = 0.640 ug/g dw) are similar to lead concentrations measured in eggs of terns, gulls and black skimmers from colonies on the Atlantic coast of New Jersey (range from 0.011 ug/g dw - 1.15 ug/g dw, depending on the species; Burger 2002), while lead concentrations measured in pelican eggs from 2005 tended to be slightly higher (<0.04 ug/g dw - 2.72 ug/g dw).

The lead concentrations measured in eggs of pelicans from WAI may be typical for seabirds that nest on islands near heavily developed areas. Historically, significant releases of lead were associated with leaded gasoline, lead-based paint, lead-containing pesticides, lead-containing ammunition, and lead fishing weights and sinkers. While most of the major uses have ceased, the lead that was released remains in the environment. There continue to be releases with municipal wastewater discharges, industrial discharges, untreated urban runoff, and atmospheric emissions (ATSDR 2007b). Lead is generally present at elevated levels in sediments of the SCB, and particularly around Los Angeles, which is the largest metropolitan area on the west coast of the United States (Mearns et al. 1991; Schiff 2000). Lead levels may be elevated in SCB fish consumed by pelicans that nest on WAI, but whether such is the case is unknown. Lead levels measured in mussels demonstrate that the sediment-borne lead enters the food web and is accumulated in the tissues of exposed organisms (Mearns et al. 1991). However, while lead may be bioaccumulated by directly exposed organisms, biomagnification in food web organisms is negligible, and concentrations in carnivorous fish, such as those consumed by pelicans are typically lower than concentrations measured in lower trophic organisms (ATSDR 2007b). Absent data, lead levels in fish consumed by WAI pelicans are assumed to be somewhat elevated, and they may or may not be reflective of local influences.

Lead is a nonessential element with detrimental effects at any level of exposure (Eisler 1988; ATSDR 2007b; Pain 1996). Adverse effects in birds can be as severe as acute lethality after consuming lead shot, lead sinkers and lead-based paint chips. Sublethal effects of lead exposure include alterations in the hematopoetic system (causing symptoms of anemia) and bone structure, impaired kidney function, anorexia, poor growth or weight loss, central nervous system damage, and reduced egg production and eggshell thinning (Eisler 1988; USEPA 2005). Lead exposure by avian embryos can

result in embryo mortality and gross deformities (Birge and Roberts 1976). Exposure as an embryo may also result in altered immune system function measured as antibody production (Bunn et al. 2000) and brain development (Nyholm 1998).

The vast majority of data on toxic lead levels relate adverse effects to concentrations in blood, liver, kidney and bone (Franson 1996). Once absorbed, lead is deposited primarily in the kidney and liver and is accumulated over the long-term in bones (Pain 1996). While there is some maternal transfer of lead to eggs, lead does not accumulate in eggs, and therefore does not appear to reach levels that can be associated with observable adverse effects in wild birds. Reports of laboratory studies relating the lead concentrations in eggs to adverse effects are sparse as well. One study was located. Results of an egg injection study by Birge and Roberts (1976) on domestic chickens demonstrated a dose-response relationship between the lead concentration in yolk and adverse effects that included embryo mortality, and gross deformities in chicks that survived past hatching. Statistical comparisons between control and exposed groups are not provided. A median effect level for mortality was evident with a lead concentration of 1 ug/g ww in yolk. That dose was also associated with teratogenic effects in 14% of the survivors. Assuming that the yolk is approximately 35% of the mass of the egg contents (Ricklefs 1977; Richards 1997), the median effect level for lead in yolk is equivalent to approximately 0.35 ug/g ww in the whole egg. The mean fresh weight concentrations of lead measured in pelican eggs for this study (0.03 ug/g fw in 1993 and 0.09 ug/g fw in 2005; Table 8) are below 0.350 ug/g ww, and as such are below median effect levels for embryo mortality in chickens. Concentrations in two individual eggs from 2005 were greater than 0.35 ug/g fw and may be sufficient to adversely affect embryo survival. Burger (2002) compared lead levels in gull and seabird eggs to concentrations reported for piscivorous birds exhibiting no apparent adverse effects, and identified a median of 0.190 ug/g ww for evaluating study results. Mean lead levels measured in pelican eggs for this study (<0.10 ug/g ww) are less than the median reported for piscivorous birds that appear unaffected by contaminants. The maximum concentration of lead measured pelican eggs for this study (0.463 ug/g ww) is within the range identified by Burger (2002) as associated with no apparent effects (0.02 ug/g ww - 6.7 ug/g ww).

Of the remainder of inorganic analytes detected in pelican eggs collected for this study (Table 8) only aluminum, arsenic, barium, copper, manganese, strontium, titanium and zinc are considered potential contaminants (excludes K, Na and S). Copper, manganese, and zinc are essential in small amounts for the function of one or more enzymes (Ohlendorf 1993; Richards 1997). Animals have mechanisms for regulating essential elements, which lowers the likelihood that essential elements will occur at toxic levels. The regulatory mechanisms can be overwhelmed if concentrations are high enough. Concentrations of these elements in WAI brown pelican eggs may be compared with concentrations measured in other seabirds (Zeeman et al. 2008) or white pelicans from a potentially stressed colony (Wiemeyer 2004), to ascertain if concentrations appear elevated.

Based on a rough comparison, concentrations of aluminum, barium, manganese, strontium and titanium measured in brown pelican eggs for this study overlap ranges reported for white pelicans at Anaho Island, Nevada (Wiemeyer 2004) and in failed eggs of terns and skimmers from south San Diego Bay (Zeeman et al. 2008). None stand out as exceptionally high or low.

Arsenic concentrations measured in pelican eggs are comparable to arsenic concentrations measured in tern and skimmer eggs from San Diego Bay, and may be typical for marine seabirds (Zeeman et al. 2008). Arsenic concentrations in WAI brown pelican eggs are greater than arsenic concentrations measured in eggs of white pelicans from Anaho Island, Nevada (<0.005 - 0.1 ug/g ww; Wiemeyer 2004). This probably reflects differences in diet as arsenic concentrations in marine fish are orders of magnitude higher than arsenic concentrations in freshwater fish (ATSDR 2007a). Dry weight based arsenic concentrations (overall mean 0.65 ug/g dw, and range 0.4 ug/g dw - 1.2 ug/g dw) are below a tentative screening level of 1.3 ug/g dw for no effects in avian eggs (USDOI 1998).

Copper was detected frequently in pelican eggs, at concentrations higher than those measured in failed to hatch skimmer eggs from San Diego Bay. In 2005, the mean for pelicans was 2.59 and range was 1.11-8.82 ug/g fw, whereas for skimmers it was 1.18 (range 0.75-2.02; Zeeman et al. 2008). Copper concentrations measured in brown pelican eggs for this study (overall mean 2.2 ug/g fw) are higher than mean copper concentrations (~1.0 ug/g fw) detected by Wiemeyer (2004) in eggs of white pelicans from Anaho Island, Nevada. A background concentration for copper in eggs of 5.5 ug/g dw was identified in the review by USDOI (1998). The lowest dry weight-based concentration for copper in pelican eggs from WAI is 5.9 ug/g dw. All of the eggs collected in 1993 and 2005 had copper concentrations greater than background. The copper concentrations in brown pelican eggs may reflect higher concentrations in the system. Copper is one of the elements that occurs at elevated concentrations in sediments along the coast of the SCB, and particularly in Santa Monica Bay (Los Angeles; Schiff 2000). Because copper is regulated by most animals, it is not clear that higher copper concentrations in sediments, and subsequently certain invertebrates, would translate into higher levels in forage fish consumed by pelicans.

Data on the effects and effect levels for copper in avian eggs are lacking (USDOI 1998). However, because copper is an essential element, it is likely that concentrations observed in pelican eggs collected for this study are below toxic concentrations.

At approximately 8 ug/g fw mean zinc concentrations measured in eggs of pelicans from WAI (Table 8) are slightly lower than means of 14 ug/g fw - 20 ug/g fw observed with failed eggs of terns and black skimmers from San Diego Bay colonies (Zeeman et al. 2008). Mean zinc concentrations measured in brown pelican eggs from WAI are within ranges reported for white pelicans from Anaho Island NWR, and are consistent with concentrations around 12 ug/g fw which is considered normal for eggs of marine birds (Eisler 1993; USDOI 1998). Zinc is an essential element, and adverse effects have been associated with both deficient and excessive exposure. Adverse reproductive effects

associated with high levels of exposure by adults include reduced egg production, reduced eggshell strength and hatchability. More subtle effects associated with lowest dietary effect level reported for domestic chickens include suppression of the immune system, but not growth of progeny (Eisler 1993). Only one study was located that related the concentration in eggs to adverse effects. Birge and Roberts (1976) conducted egg injection studies exposing embryos of domestic chickens to multiple metals, including zinc. Results of that study suggest that, like lead (previous section), zinc concentrations as low as 0.35 ug/g ww may result in embryo lethality and teratogenesis. The effect level observed by Birge and Roberts (1976) is orders of magnitude lower than what normally occurs in eggs of marine birds, or what is considered background for avian eggs in general (10 ug/g ww; USDOI 1998). Zinc is an essential element whose mobilization and transfer from storage sites to the developing embryo is regulated during development of the avian embryo (Richards 1997). It is likely that results of the study by Birge and Roberts (1976) overestimate risk from zinc, because the level and / or the timing of zinc exposure by the embryo may have been different when the zinc was injected versus when it would have been mobilized during regular developmental processes (Richards 1997).

4.0 CONCLUSIONS AND RECOMMENDATIONS

Productivity of California brown pelicans nesting on WAI has improved substantially since the late 1960's and early 1970's. As recently as 2003, productivity has been characterized by long-term averages that were evident since 1979, and punctuated by large annual fluctuations that can be attributed to food supply and/or periodically by unusual events such as oil spills, toxic algal blooms, and human disturbance (Gress et al. 2003). However, the number young fledged per nest attempt in 2003 (0.71) and the long-term average (0.65) are still below the long-term mean of 1.0 observed in brown pelican colonies outside the SCB.

Results of this study have lead to the following conclusions and recommendations.

1. While factors such as food supply may play a role in the apparently low number of pelicans fledged per nest, contaminants are present and subtle effects associated with contaminant exposure may not be completely ruled out as contributing factors.

2. Eggshell thickness for brown pelicans nesting on WAI appears to have returned to levels greater than those observed before the widespread use of DDT. This conclusion is based on results obtained with eggs collected in 2005 only, which by multiple measures were significantly thicker than eggs collected in 1993. Whether shell thicknesses observed with eggs from 2005 are artifact or reflect real changes in WAI pelicans is uncertain.

   Additional monitoring of eggshell thickness and strength is recommended to determine if results obtained in 2005 are representative of a long-term trend, to confirm that eggshell thinning is no longer a potential factor affecting

productivity of pelicans on WAI, and evaluate potential causes and physiological implications for the occurrence of unusually thicker shells.

3. Overall concentrations of bioaccumulative organic contaminants in pelican eggs have declined and the differences between 1993 and 2005 are significant, due largely to significant declines in concentrations of DDTs and PCBs. Results obtained with DDT and PCBs are consistent with a long-term slow decline evident since the early-to-mid 1970s. While concentrations are declining overall, ratios of DDE to PCBs in pelican eggs from WAI continue to reflect the influence, albeit declining, of a historical local manufacturing source of DDTs.

4. By 1993, the concentration of DDT was below thresholds associated with measurable eggshell thinning for most but not all eggs. In 2005, the concentration of DDT was below thresholds in all of the eggs. This reflects a decline over time in both the mean concentration and in the incidence of individuals with elevated levels of exposure.

5. DDTs and PCBs continue to be the dominant organic contaminants in brown pelican eggs, which is testimony to the persistence and bioaccumulation potential for these legacy contaminants in environmental media. The presence of PBDEs at concentrations exceeded only by DDTs and PCBs reflects the pervasiveness and bioaccumulation potential for these newer use compounds in marine food webs. Unlike DDTs and PCBs, the temporal trend for concentrations of PBDEs is uncertain.

6. Concentrations of PBDEs measured in pelican eggs are between a no effect level and a low effect level for reduced egg size and for shell thinning in sensitive avian species.

   Given the uncertainty about the direction that PBDE levels are going, and levels associated with adverse effects, continued monitoring for PBDEs is recommended as part of efforts to confirm that contaminants are not limiting pelican productivity.

7. While numerous legacy OC compounds other than DDT and PCBs were detected in pelican eggs, none were present at concentrations that individually exceeded thresholds for adverse effects. Whether OC compounds other than DDT and PCBs may exert adverse effects as a mixture is unknown. Although low, concentrations of hexachlorobenzene, tetrachlorobenzene and pentachloroanisole increased between 1993 and 2005.

   Given that concentrations of some legacy OC pesticides increased between 1993 and 2005, continued monitoring for OC compounds is recommended as part of efforts to confirm that contaminants are not limiting pelican productivity

8. Brown pelican eggs were analyzed for 28 inorganic compounds, nineteen of which were detected in more than 50% of the 30 eggs that were analyzed. Due to the paucity of data, the implications of observed concentrations for most of the metals are unknown. However, results of this study provide data on numerous metals that may help with interpretation of data from future studies.

9. Concentrations of nearly all the detected metals, including mercury and selenium which are most frequently associated with adverse effects, were below levels associated with proximity to sources or adverse effects.

10. Calcium, magnesium and phosphorus were the only elements for which concentrations observed in 2005 were significantly higher than concentrations observed in 1993. The apparent increase in calcium, magnesium and phosphorus concentrations can be attributed to mobilization of these elements that occurs during the later stages of embryo development.

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